

CHEMICAL PROCESSING HANDBOOK

edited by

John J. McKetta

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Chemical Processing Handbook

Edited by
John J. McKetta

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Preface

We are pleased to present many chemical processes in an alphabetically organized, easy-to-read and understandable manner. This handbook covers up-to-date processing operations in the chemical industry. Each section is written by a world expert in that particular area in such a manner that it is easily understood and applied. Each professional practicing engineer or industrial chemist involved in chemical processing should have a copy of this book on his or her working shelf.

Each of the processing articles contains information on plant design as well as significant chemical reactions. Wherever possible, shortcut methods of calculations are included, along with nomographic methods of solutions. In the front of the book are two convenient sections that will be very helpful to the reader: (1) conversion to and from SI units and (2) cost indexes that will enable the reader to update any cost information.

As editor, I am grateful for all the help I have received from the great number of authors who have contributed to this book. I am also grateful to the huge number of readers who have written to me with suggestions of topics to be included.

JOHN J. MCKETTA

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Conversion to SI Units

To convert from	To	Multiply by
acre	square meter (m ²)	4.046×10^3
angstrom	meter (m)	1.0×10^{-10}
are	square meter (m ²)	1.0×10^2
atmosphere	newton/square meter (N/m ²)	1.013×10^5
bar	newton/square meter (N/m ²)	1.0×10^5
barrel (42 gallon)	cubic meter (m ³)	0.159
Btu (International Steam Table)	joule (J)	1.055×10^3
Btu (mean)	joule (J)	1.056×10^3
Btu (thermochemical)	joule (J)	1.054×10^3
bushel	cubic meter (m ³)	3.52×10^{-2}
calorie (International Steam Table)	joule (J)	4.187
calorie (mean)	joule (J)	4.190
calorie (thermochemical)	joule (J)	4.184
centimeter of mercury	newton/square meter (N/m ²)	1.333×10^3
centimeter of water	newton/square meter (N/m ²)	98.06
cubit	meter (m)	0.457
degree (angle)	radian (rad)	1.745×10^{-2}
denier (international)	kilogram/meter (kg/m)	1.0×10^{-7}

dram (avoirdupois)	kilogram (kg)	1.772×10^{-3}
dram (troy)	kilogram (kg)	3.888×10^{-3}
dram (U.S. fluid)	cubic meter (m ³)	3.697×10^{-6}
dyne	newton (N)	1.0×10^{-5}
electron volt	joule (J)	1.60×10^{-19}
erg	joule (J)	1.0×10^{-7}
fluid ounce (U.S.)	cubic meter (m ³)	2.96×10^{-5}
foot	meter (m)	0.305
furlong	meter (m)	2.01×10^2
gallon (U.S. dry)	cubic meter (m ³)	4.404×10^{-3}
gallon (U.S. liquid)	cubic meter (m ³)	3.785×10^{-3}
gill (U.S.)	cubic meter (m ³)	1.183×10^{-4}
grain	kilogram (kg)	6.48×10^{-5}
gram	kilogram (kg)	1.0×10^{-3}
horsepower	watt (W)	7.457×10^2
horsepower (boiler)	watt (W)	9.81×10^3
horsepower (electric)	watt (W)	7.46×10^2
hundred weight (long)	kilogram (kg)	50.80
hundred weight (short)	kilogram (kg)	45.36
inch	meter (m)	2.54×10^{-2}
inch mercury	newton/square meter (N/m ²)	3.386×10^3
inch water	newton/square meter (N/m ²)	2.49×10^2

kilogram force

newton (N)

9.806

To convert from	To	Multiply by
kip	newton (N)	4.45×10^3
knot (international)	meter/second (m/s)	0.5144
league (British nautical)	meter (m)	5.559×10^3
league (statute)	meter (m)	4.83×10^3
light year	meter (m)	9.46×10^{15}
liter	cubic meter (m ³)	0.001
micron	meter (m)	1.0×10^{-6}
mil	meter (m)	2.54×10^{-6}
mile (U.S. nautical)	meter (m)	1.852×10^3
mile (U.S. statute)	meter (m)	1.609×10^3
millibar	newton/square meter (N/m ²)	100.0
millimeter mercury	newton/square meter (N/m ²)	1.333×10^2
oersted	ampere/meter (A/m)	79.58
ounce force (avoirdupois)	newton (N)	0.278
ounce mass (avoirdupois)	kilogram (kg)	2.835×10^{-2}
ounce mass (troy)	kilogram (kg)	3.11×10^{-2}
ounce (U.S. fluid)	cubic meter (m ³)	2.96×10^{-5}
pascal	newton/square meter (N/m ²)	1.0
peck (U.S.)	cubic meter (m ³)	8.81×10^{-3}
pennyweight	kilogram (kg)	1.555×10^{-3}
pint (U.S. dry)	cubic meter (m ³)	5.506×10^{-4}

pint (U.S. liquid)	cubic meter (m ³)	4.732×10^{-4}
poise	newton second/square meter (N . s/m ²)	0.10
pound force (avoirdupois)	newton (N)	4.448
pound mass (avoirdupois)	kilogram (kg)	0.4536
pound mass (troy)	kilogram (kg)	0.373
poundal	newton (N)	0.138
quart (U.S. dry)	cubic meter (m ³)	1.10×10^{-3}
quart (U.S. liquid)	cubic meter (m ³)	9.46×10^{-4}
rod	meter (m)	5.03
roentgen	coulomb/kilogram (c/kg)	2.579×10^{-4}
second (angle)	radian (rad)	4.85×10^{-6}
section	square meter (m ²)	2.59×10^6
slug	kilogram (kg)	14.59
span	meter (m)	0.229
stoke	square meter/second (m ² /s)	1.0×10^{-4}
ton (long)	kilogram (kg)	1.016×10^3
ton (metric)	kilogram (kg)	1.0×10^3
ton (short, 2000 pounds)	kilogram (kg)	9.072×10^2
torr	newton/square meter (N/m ²)	1.333×10^2
yard	meter (m)	0.914

Bringing Costs up to Date

John J. McKetta

Cost escalation via inflation bears critically on estimates of plant costs. Historical costs of process plants are updated by means of an escalation factor. Several published cost indexes are widely used in the chemical process industries:

Nelson-Farrar Cost Indexes (Oil and Gas J.), quarterly

Marshall and Swift (M&S) Equipment Cost Index, updated monthly

CE Plant Cost Index (Chemical Engineering), updated monthly

ENR Construction Cost Index (Engineering News-Record), updated weekly

All these indexes were developed with various elements, such as material availability and labor productivity, taken into account. However, the proportion allotted to each element differs with each index. The differences in overall results of each index are due to uneven price changes for each element. In other words, the total escalation derived by each index will vary because different bases are used. The engineer should become familiar with each index and its limitations before using it.

Table 1 compares the CE Plant Index with the M&S Equipment Cost

TABLE 1 Chemical Engineering and Marshall and Swift Plant and Equipment Cost Indexes since 1950

Year	CE Index	M&S Index	Year	CE Index	M&S Index
1950	73.9	167.9	1971	132.3	321.3
1951	80.4	180.3	1972	137.2	332.0
1952	81.3	180.5	1973	144.1	344.1
1953	84.7	182.5	1974	165.4	398.4
1954	86.1	184.6	1975	182.4	444.3
1955	88.3	190.6	1976	192.1	472.1
1956	93.9	208.8	1977	204.1	505.4
1957	98.5	225.1	1978	218.8	545.3
1958	99.7	229.2	1979	238.7	599.4
1959	101.8	234.5	1980	261.2	659.6
1960	102.0	237.7	1981	297.0	721.3
1961	101.5	237.2	1982	314.0	745.6
1962	102.0	238.5	1983	316.9	760.8
1963	102.4	239.2	1984	322.7	780.4
1964	103.3	241.8	1985	325.3	789.6
1965	104.2	244.9	1986	318.4	797.6
1966	107.2	252.5	1987	323.8	813.6
1967	109.7	262.9	1988	342.5	852.0
1968	113.6	273.1	1989	355.4	895.1
1969	119.0	285.0	1990	357.6	915.1
1970	125.7	303.3	1991	361.3	930.6

TABLE 2 Nelson-Farrar Inflation Refinery Construction Indexes since 1946
(1946 = 100)

Date	Materials Component	Labor Component	Miscellaneous Equipment	Nelson-Farrar Inflation Index
1946	100.0	100.0	100.0	100.0
1947	122.4	113.5	114.2	117.0
1948	139.5	128.0	122.1	132.5
1949	143.6	137.1	121.6	139.7
1950	149.5	144.0	126.2	146.2
1951	164.0	152.5	145.0	157.2
1952	164.3	163.1	153.1	163.6
1953	172.4	174.2	158.8	173.5
1954	174.6	183.3	160.7	179.8
1955	176.1	189.6	161.5	184.2
1956	190.4	198.2	180.5	195.3
1957	201.9	208.6	192.1	205.9
1958	204.1	220.4	192.4	213.9
1959	207.8	231.6	196.1	222.1
1960	207.6	241.9	200.0	228.1
1961	207.7	249.4	199.5	232.7
1962	205.9	258.8	198.8	237.6
1963	206.3	268.4	201.4	243.6
1964	209.6	280.5	206.8	252.1
1965	212.0	294.4	211.6	261.4
1966	216.2	310.9	220.9	273.0
1967	219.7	331.3	226.1	286.7
1968	224.1	357.4	228.8	304.1
1969	234.9	391.8	239.3	329.0
1970	250.5	441.1	254.3	364.9
1971	265.2	499.9	268.7	406.0
1972	277.8	545.6	278.0	438.5
1973	292.3	585.2	291.4	468.0
1974	373.3	623.6	361.8	522.7
1975	421.0	678.5	415.9	575.5
1976	445.2	729.4	423.8	615.7
1977	471.3	774.1	438.2	653.0
1978	516.7	824.1	474.1	701.1
1979	573.1	879.0	515.4	756.6
1980	629.2	951.9	578.1	822.8
1981	693.2	1044.2	647.9	903.8
1982	707.6	1154.2	622.8	976.9
1983	712.4	1234.8	656.8	1025.8
1984	735.3	1278.1	665.6	1061.0
1985	739.6	1297.6	673.4	1074.4
1986	730.0	1330.0	684.4	1089.9
1987	748.9	1370.0	703.1	1121.5
1988	802.8	1405.6	732.5	1164.5
1989	829.2	1440.4	769.9	1195.9
1990	832.8	1487.7	797.5	1225.7
1991	832.3	1533.3	827.5	1252.9

Index. Table 2 shows the Nelson-Farrar Inflation Petroleum Refinery Construction Indexes since 1946. It is recommended that the CE Index be used for updating total plant costs and the M&S Index or Nelson-Farrar Index for updating equipment costs. The Nelson-Farrar Indexes are better suited for petroleum refinery materials, labor, equipment, and general refinery inflation.

Since

$$C_B = C_A(B/A)^n \quad (1)$$

Here, A = the size of units for which the cost is known, expressed in terms of capacity, throughput, or volume; B = the size of unit for which a cost is required, expressed in the units of A; n = 0.6 (i.e., the six-tenths exponent); CA = actual cost of unit A; and CB = the cost of B being sought for the same time period as cost CA.

To approximate a current cost, multiply the old cost by the ratio of the current index value to the index at the date of the old cost:

$$C_B = C_A I_B / I_A \quad (2)$$

Here, CA = old cost; IB = current index value; and IA = index value at the date of old cost.

Combining Eqs. (1) and (2),

$$C_B = C_A(B/A)^n(I_B/I_A) \quad (3)$$

For example, if the total investment cost of plant A was \$25,000,000 for 200-million-lb/yr capacity in 1974, find the cost of plant B at a throughput of 300 million lb/yr on the same basis for 1986. Let the sizing exponent, n, be equal to 0.6.

From Table 1, the CE Index for 1986 was 318.4, and for 1974 it was 165.4. Via Eq. (3),

$$\begin{aligned} C_B &= C_A(B/A)^n(I_B/I_A) \\ &= 25.0(300/200)^{0.6}(318.4/165.4) \\ &= \$61,200,000 \end{aligned}$$

Chemicals from Natural Gas

Duffer B. Crawford,
Charles A. Durr,
James A. Finneran,
and William Turner

Natural gas may be converted to a variety of industrial chemicals, petrochemicals, and fertilizers. These are indicated along with the processes used in their manufacture. More detailed information, such as yield data and scale of commercial production capacity, are identified for ammonia and its fertilizer derivatives.

Introduction

Natural gas is an excellent feedstock in the chemical industry. Figure 1 indicates the components that can be separated from natural gas in a typical processing plant. This article will review the first and second step chemical derivatives that are manufactured from methane, ethane, propane (LPG), and butane. However, the primary emphasis is on the chemical products that are

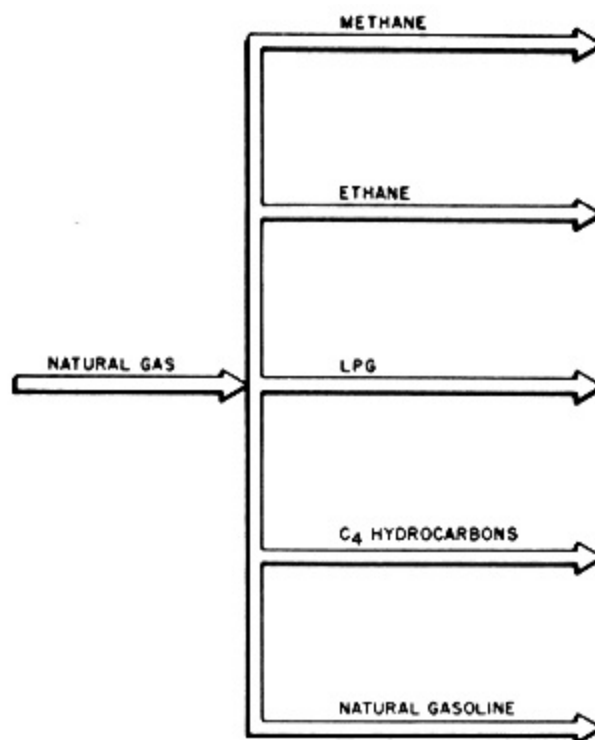


Fig. 1

manufactured from methane; i.e., the "vertical integration" of chemicals and fertilizers that are produced from methane is presented in more detail.

The use of natural gas as a feed to chemical plants is based primarily upon the chemical production and consumption experienced in the United States. The statistics presented do not directly apply to the rest of the world; however, these statistics are useful because they demonstrate the utilization of natural gas in a country where, until recently, natural gas was considered to be plentiful. Also, the utilization of natural gas as a chemical feed is more developed in the United States than in any other country in the world.

Natural Gas

Natural gas is a mixture of hydrocarbons ranging from methane to pentane or heavier. These hydrocarbons are mostly paraffins but do include a small amount of naphthenes. Natural gas is highly desirable because it is a relatively clean fuel as well as an excellent feedstock for the chemical industry. Natural gas may be steam reformed for the production of ammonia which serves as a fertilizer or as the main building block in the synthesis of other fertilizers and chemicals.

The natural gas components heavier than methane are usually separated via a cryogenic fractionating step prior to use as a petrochemical feedstock. The ethane may be "cracked" to form ethylene; likewise, the propane and butane may be cracked to ethylene/propylene or can be used as a fuel. The heaviest components, known as natural gasoline, may be used in gasoline blending, may be charged to a refinery as supplemental feed, or may be cracked to form ethylene/propylene and its by-products.

Natural Gas Usage

A recent study [1] estimates that 2.6% of the natural gas consumption in the United States is used by the petrochemical industry as a feedstock while another 4.6% is used as a fuel. Thus the consumption of natural gas for petrochemicals is not large. However, for the petrochemical industry, natural gas is its major supplier of fuel and feedstock. Table 1 shows the results of a study for the Federal Energy Administration in the United States. This study was made to determine the consumption of fuels and petroleum products within the chemical industry. Thirty-seven chemicals were chosen to represent the broad range of chemicals that are actually manufactured; these represent 63% of the total process and feedstock energy consumption for all chemicals in the United States.

Table 1 indicates that natural gas supplies 49.9% of the total energy requirements for the chemicals while LPG supplies another 23.7%. Thus it is obvious that, even though the natural gas and LPG used for chemicals is only a small portion of the available supply in the United States, they are vital as a source of fuel and feedstock energy to the petrochemical industry.

TABLE 1 Consumption of Fuels and Feedstocks in the Chemical Industry of the United States, 1973 (based on 37 selected chemicals) [2]

Source of Energy	Process Energy (%)	Feedstock Energy (%)	Total Energy (%)
Dry natural gas	34.2	15.7	49.9
Coal	3.9	Minor	3.9
Residual fuel oil	0.8		0.8
Distillate oil	1.3		1.3
Fuels	0.7		0.7
Ethane/propane (LPG)		23.7	23.7
Naphtha and other		14.7	14.7
Benzene		5.0	5.0
Total	40.9	59.1	100.0

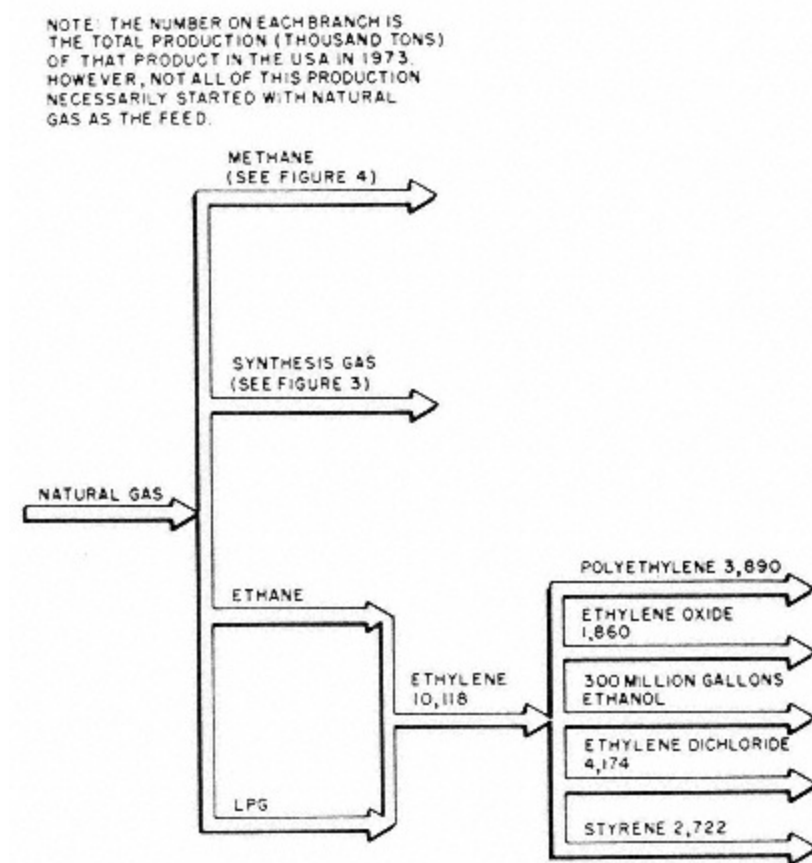


Fig. 2

Natural Gas Processing Plants

Usually "wet" natural gas is processed to separate the heavy paraffins from the methane. This may be done via an absorption process, a refrigerated absorption process, or a cryogenic process. In general, if a high recovery is desired only for the propane and heavier components, the absorption process is used; for an intermediate level of ethane recovery, the refrigerated absorption process; and for high ethane recovery, a cryogenic process would be used.

During 1971, 80% of the available natural gas in the United States was processed in natural gas processing plants. During this processing, about 51 million t of natural gas liquids (NGL) were extracted. About 47% of this NGL was exported for use in refineries while the remainder was for direct use as fuel, power, and feedstock. About 17.6 million t were used for a chemical feedstock, mostly to ethylene plants.

Components of Natural Gas As a Chemical Feed

Figure 2 shows the basic "chemical tree" of chemicals, building blocks, etc. that can be produced from natural gas. The "chemical tree" will be developed to indicate the first and second stage chemical derivatives using methane, ethane, LPG, and C₄ hydrocarbon as the feedstock. However, more detail will be presented covering the primary, secondary, and in some cases the tertiary derivatives from methane.

Ethane and LPG

Almost all of the ethane and LPG that is used as a chemical feed is used in the manufacture of ethylene. Although ethylene has very few direct end uses, it is one of the most important chemical building blocks in producing such products as polyethylene, ethylene oxide, ethanol, and styrene. This importance derives from the reactivity of the double bond and due to its capability to copolymerize with itself and other monomers; these properties have resulted in the large volume production of a wide variety of ethylene derivatives. The consumption pattern of ethylene is shown in Table 2 from which it is apparent that polyethylene is the major consumer of ethylene followed by ethylene oxide and ethylene dichloride. High- and low-density polyethylene is used in the manufacture of films and in injection molding. Ethylene oxide is used in the production of glycol ethers, ethylene glycols, and ethanolamines.

Table 3 lists the type, number, and capacity of ethylene or ethylene derivative plants that are either under construction, planned, or proposed in the world as of February 1975.

TABLE 2 Consumption of Ethylene in the United States in 1974 [3]

	%
Polyethylene (low-density)	27.9
Polyethylene (high-density)	12.7
Ethylene oxide (and glycol)	19.5
Ethylene dichloride	14.0
Ethanol	5.5
Styrene (via ethyl benzene)	8.5
Others	11.9
Total	100.0

Today, most of the ethylene is made by the thermal cracking of any naphthenic or paraffinic hydrocarbon heavier than methane (see Table 4); the amount of ethylene and by-products formed will depend upon the molecular weight of the feed. As the molecular weight increases above that of ethane, the amount of by-products increases dramatically. Thus the simplest and least expensive plant will result when ethane is used as a feedstock. Heavier feeds, such as gas oil and naphtha, are also used in making ethylene/propylene and its by-products. In this case the market values of the by-products are important in determining the plant's economic viability.

Ethane and LPG are preferred feeds for chemical companies that are not fully integrated to market the by-products produced with heavier feeds. The major trend in recent years in the United States has been toward the use of heavier feeds such as naphtha or gas oil because of the unavailability of ethane and LPG. This trend has increased the proportion of ethylene that has been manufactured by oil companies. This is mainly because the oil companies have better access to the available feed and because they are also in a better position to sell the various by-products.

TABLE 3 Ethylene-Based Plants (under construction, planned, or proposed) in the World as of February 1975 [4]

Product	Number of New Plants	Total New Capacity (thousand tons/yr)
Ethylene	76	19,284
Polyethylene	77	5,970
Ethylene oxide	18	1,240
Ethylene glycol	13	731
Styrene	16	2,223
Polystyrene	16	676
Ethylene dichloride	3	485

TABLE 4 Ethylene Production from Various Feedstocks in the United States, 1974 [5]

Feedstock	Thousand Tons/Year
Ethane	5,580
LPG	3,040
Naphtha	680
Gas oil	953
Total	10,253

In Japan and Europe the lack of natural gas as a source of ethane/LPG forced olefin producers to select naphtha as their main feedstock. However, this trend may be modified in Europe if the North Sea gas contains significant amounts of ethane/LPG components.

Propane and Butane Hydrocarbons

The chemical use of these hydrocarbons has been growing in recent years. Propane is obtained from the light end of crude oil or the heavy end (NGL) extracted from natural gas along with ethane and butane. Approximately 30% of the propane produced in the United States is used as a chemical feed, primarily in producing ethylene/propylene. The remaining 70% is used in the energy sector of the economy [6]; i.e., industrial fuel, utility gas, and producing SNG.

About one-third of the butane produced today comes from natural gas liquids; the remainder comes from refineries. The chemical applications for butanes are only minor when compared to the amounts used for gasoline production. About 8% is used as a chemical raw material. For example, n-butane may be dehydrogenated to produce butadiene (primary derivative) or n-butenes. Isobutane is also consumed as a chemical feed. However, only about 2% of it is used in this manner. The remainder is used in alkylation.

Synthesis Gas

Natural gas and other hydrocarbons are used to make synthesis gas; i.e., carbon monoxide and hydrogen. This synthesis gas is used in the manufacture of ammonia, methanol, phosgene, and oxo alcohols, which in turn are used in

the manufacture of many other fertilizers and industrial chemicals. Depending upon which product is desired, the composition of the synthesis gas is selected in order to have the proper ratio of hydrogen and carbon monoxide. For example, to produce methanol, the ratio is $2\text{H}_2:1\text{CO}$ (or $3\text{H}_2:1\text{CO}_2$); for the oxo reaction, $1\text{H}_2:1\text{CO}$. For ammonia, the required ratio of $3\text{H}_2:1\text{N}_2$ is satisfied by obtaining the hydrogen from the hydrocarbon and the nitrogen from air that is introduced into the process. In making phosgene, formic acid, and oxalic acid, only the carbon monoxide is required; for producing peroxide and in hydrogenation processes, only the hydrogen is required. Synthesis gas can also be produced from coke oven gas, coal gas, or the electrolysis of water. However,

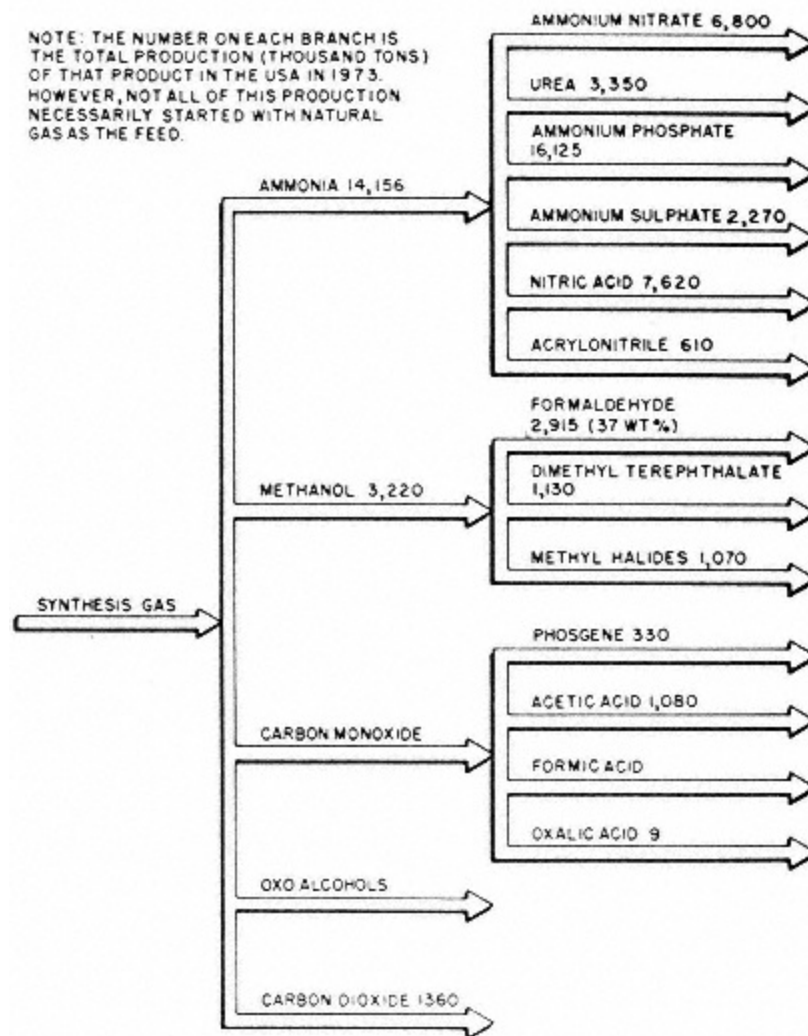


Fig. 3

TABLE 5 Synthesis Gas-Based Plants (under construction, planned, or proposed) in the World as of February 1975 [4]

Product	Number of New Plants	Total New Capacity (thousand tons/yr)
Ammonia	90	27,400
Ammonium nitrate	17	4,247
Urea	61	23,000
Nitric acid	27	5,775
Ammonium sulfate	2	333
Acrylonitrile	16	1,089
Methanol	20	2,772
Formaldehyde	16	440
Carbon monoxide	Not available	Not available
Phosgene	2	75
Oxo alcohols	3	130

the main methods practiced today are the steam reforming or partial oxidation of hydrocarbons. In particular, steam reforming is the primary method.

Figure 3 shows the chemical products and/or intermediates that can be manufactured from synthesis gas. This section of this article will review these chemicals and their derivatives as shown in the figure. Table 5 lists the type, number, and capacity of synthesis gas-based plants that are either under construction, planned, or proposed in the world.

Ammonia

Ammonia is the second largest volume chemical produced in the United States; second only to sulfuric acid. Its great value stems from the fact that it is a raw material for fertilizers, explosives, synthetic fibers, and plastics. Table 6 shows the consumption breakdown for ammonia. This indicates that 76.3% of the ammonia consumed in the United States is used directly as a fertilizer or is converted into another fertilizer. In fact, almost all nitrogen fertilizers are manufactured from anhydrous ammonia. Notice that 26.6% of the ammonia consumption is applied directly to the soil in the liquid form. This consumption pattern is unique to the United States. Most other countries first convert all the ammonia into a solid fertilizer before it is applied to the soil.

Most of the ammonia production in the world is based on steam-hydrocarbon reforming; this accounts for about 75 to 80% of world production with 60 to 65% of this using natural gas as the feed. It is expected that this percentage will hold for the near-term future. However, on a long-range basis it is expected that heavier feeds and coal will increase their percentage as a feedstock, gradually displacing natural gas.

TABLE 6 Major Domestic Uses and Consumption Distribution of Ammonia in the United States in 1972 [7]

Ammonia and Derivatives	Consuming Areas		
	Fertilizers (%)	Other (%)	Total (%)
Ammonia, direct application ^a	26.6		26.6
Ammonium nitrate (AN)	17.0	4.0	21.0
Ammonium phosphate	11.2		11.2
Urea	10.1	2.4	12.5
Ammonium sulfate	5.9		5.9
Nitric acid for non-AN uses	1.1	5.8	6.9
Nitrogen solutions and mixed fertilizers	4.4		4.4
Acrylonitrile		2.2	2.2
Other		9.3	9.3
Total	76.3	23.7	100.0

^aAs anhydrous or aqua ammonia.

In order to produce the hydrogen for ammonia production, the raw synthesis gas from steam reforming, containing carbon monoxide, carbon dioxide, and hydrogen, must be further processed. First, the carbon monoxide plus steam is shifted to produce more carbon dioxide and hydrogen. Second, the carbon dioxide is removed from the gas by a liquid absorption system. Third, the remaining traces of CO are removed by converting it back to methane. Since nitrogen (in the form of air) was added to the raw synthesis gas during its generation, the final output is the required synthesis gas containing the ratio 3H₂:1N₂ necessary for ammonia production.

As indicated previously, most ammonia is converted into a solid fertilizer, such as urea or ammonium nitrate, before it is applied to the soil. It is worthwhile to examine how and why these nitrogen conversion steps are employed. In particular, ammonium nitrate, ammonium phosphate, urea, and ammonium sulfate will be examined. In addition, the production of nitric acid and acrylonitrile from ammonia will be covered.

Table 7 gives production information about ammonia and its derivatives. The column labeled "Feed" lists the feedstocks necessary to manufacture the product. The next column indicates the amount of feed required to produce 1 ton of product. The fourth column gives the amount of natural gas required to produce a ton of product. For example, 965.4 normal m³ of natural gas are required to produce 1 ton of ammonia. In the case of the ammonia derivative products, the natural gas consumption was determined by multiplying the ammonia requirement per ton of product by 965.4 normal m³/ton of ammonia. Thus this indicates the amount of natural gas that must be fed to the ammonia plant to produce the fertilizer. Of course, ammonia (and nitric acid) is an

intermediate product in this case. This column of the table is interesting because these numbers can be used as coefficients in an equation to determine the approximate net output for each product in a fertilizer complex:

$$X = 965.4(A) + 424.8(AN) + 214.3(AP) + 559.9(U) + 253.9(AS) + 273.2(NA)$$

where X = natural gas feed to ammonia plant (m³/d)

A = net production of ammonia (tons/d)

AN = net production of ammonium nitrate
(tons/d)

AP = net production of ammonium phosphate
(tons/d)

U = net production of urea (tons/d)

AS = net production of ammonium sulfate
(tons/d)

NA = net production of nitric acid (tons/d)

This equation will determine the possible blend of product outputs in a nitrogen fertilizer complex when the feedstock is limited to X m³/d of natural gas. The equation assumes that natural gas is used to supply the process energy for the ammonia plant and that some other fuel is used in the ammonia derivative plants. Also, the above equation assumes that sufficient carbon dioxide is generated in the ammonia plant to supply the requirement for the urea plant. The last column in Table 7 gives the capacity of commercial producing plants for each of the products.

TABLE 7 Production of Ammonia Derivative Fertilizers and Chemicals

Product	Feed	Ton Feed Ton Product	Normal Cubic Meter Gas per Ton Product	Commercial Production Capacity (tons/d)
Ammonia	Natural gas		965.4	10001500
Ammonium nitrate	Ammonia	0.215	207.6	1400
	Nitric acid (100%)	0.795	<u>217.2</u> 424.8	
Ammonium phosphate	Ammonia	0.22	214.3	1500
	Phosphoric acid (52%)	0.660		
Urea	Ammonia	0.580	559.9	1725
	Carbon dioxide	0.770		
Ammonium	Ammonia	0.263	253.9	1000

sulfate	Sulfuric acid (98%)	0.767		
Nitric acid (100%)	Ammonia	0.283	273.2	1100

aBased on natural gas having a lower heating value of 37,266 kJ per normal m3. This column gives the amount of natural gas that must be fed to a typical existing ammonia plant in order to produce 1 t of product.

Ammonium Nitrate. Ammonium nitrate is the largest solid fertilizer use for ammonia. About 84% (1973) of this ammonium nitrate is used in the United States as a fertilizer while the remainder is used in ammonium nitrate-based explosives.

Ammonium nitrate is made by the neutralization of nitric acid with ammonia. Since ammonia is also required to make nitric acid, the general arrangement is that an ammonia, nitric acid, and ammonium nitrate plant will be located at the same site. Also, the integral production of urea, ammonia, ammonium nitrate, and nitric acid may be accomplished in order to produce a urea-ammonium nitrate fertilizer solution for direct application to the soil. The 83 to 85% ammonium nitrate solution from the plant may be sold in the liquid form or may be converted into a solid by prilling or another such technique.

Ammonium nitrate and urea can both be used to supply nitrogen as a nutrient to the soil. Several factors must be considered in choosing the best fertilizer for a specific situation. For example, ammonium nitrate has an advantage in that about one-half of its nitrogen is in the nitrate form; this nitrate is quick acting and is good when the crop needs a quick supply of nutrient. This occurs because most plants assimilate the nitrogen in the nitrate form. However, urea has an advantage over ammonium nitrate because urea does not leach out of porous soils as easily as ammonium nitrate does. Thus more nitrogen nutrient may be absorbed by the plants in the case of urea. The best fertilizer will then depend upon the specific situation. However, the trend in the last decade has been that the ammonium nitrate growth pattern has slowed down considerably due to the fact that the less expensive nitrogen compounds such as urea or anhydrous ammonia have cut into the demand for ammonium nitrate.

Urea. Urea is a large consumer of ammonia. Most of the urea consumed in the United States is used for fertilizer; the remainder is for livestock feed, resins, etc.

Urea is manufactured by the dehydration of ammonium carbamate which, in turn, is made from ammonia and carbon dioxide. Since carbon dioxide is a waste stream from the synthesis gas preparation step (steam-methane reforming) in an ammonia plant, almost all urea plants are located next to ammonia plants.

The type of desired product from the fertilizer complex decides the type of urea process that is used. A "once thru" process is used when small amounts of urea are required for complexes producing an ammonium nitrate-urea solution fertilizer. In this case the ammonia-rich off gas from the urea plant is used in nitric acid and ammonium nitrate production. A "total recycle" process is employed when solid urea is the main product. In this situation the off gases are completely recycled to produce the maximum amount of urea from the ammonia feed. As indicated previously, urea is taking up some of the ammonium nitrate market because it is cheaper to manufacture and because it does not leach out of sandy soils easily. Also, urea has the highest nitrogen content (46% N) of any ammonium derivative fertilizer. Thus it is easier to transport and apply to the soil.

Urea did not become a major fertilizer for many years because of the corrosion problems associated with urea and ammonium

carbamate. However, engineering improvements have minimized these problems to such an extent that urea is the fastest increasing fertilizer being produced today.

Ammonium Phosphate and Sulfate. Ammonium phosphate is manufactured from the reaction between ammonia and phosphoric acid. Almost 100% of the ammonium phosphate produced in the United States is used in fertilizers. Most of the ammonium phosphate produced is made in the binutrient form and is then mixed with potash to make a complete mixed fertilizer. Diammonium phosphate (18-46-0) is the leading grade in the United States and accounts for about 80% (1973) of the total production of ammonium phosphates [8].

Ammonium sulfate is also used mostly as a fertilizer. It is important both for its sulfur and nitrogen content. Ammonium sulfate is made by neutralizing ammonia with sulfuric acid and then evaporating the water in a crystallization step. This fertilizer is also obtained as a by-product in many processes. For example, ammonium sulfate is formed during the ammonia scrubbing with sulfuric acid during coke gas cleanup. Also, in the manufacture of acrylates and caprolactam, ammonium sulfate is produced as a by-product.

Ammonium sulfate is low in nitrogen content (21%). However, its sulfur content (23%) makes it desirable for soil requiring sulfur fertilization. Also, it is helpful on alkaline soils because of its acidity.

Nitric Acid. Nitric acid consumes about 28% of the ammonia produced in the United States. Of this nitric acid, about 75% is converted directly into ammonium nitrate. The remaining 25% is used in making explosives, adipic acid, isocyanates, potassium nitrate, and various fertilizers.

Nitric acid is made by the oxidation of ammonia to nitrogen oxide, which in turn is oxidized to nitrogen dioxide; this nitrogen dioxide is then reacted with water to form nitric acid. Most nitric acid is produced in the concentration range of 54 to 60% which is acceptable for the production of ammonium nitrate. However, nitric acid of 93% concentration must be employed for producing explosives and isocyanates. In order to produce the stronger acids, some method such as dehydrating with sulfuric acid must be used.

Acrylonitrile. Most acrylonitrile in the United States is produced by the reaction of ammonia with propylene via the Sohio process; this method has replaced the previous one of catalytically reacting acetylene with hydrogen cyanides. In 1973, most of the acrylonitrile production was consumed by acrylic fibers, ABS (acrylonitrile-butadiene-styrene), SAN (styrene-acrylonitrile) resin, nitrile elastomers, etc.

Methanol

Table 8 shows the consumption pattern of methanol in the United States in 1973. As can be seen in the table, about 39% of the methanol produced is a captive intermediary for

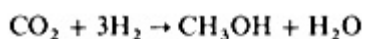
formaldehyde production. In fact, almost all the major producers of formaldehyde also produce methanol.

TABLE 8 Methanol Consumption in the United States (1973) [3]

Formaldehyde	39
Solvent useage	8
Dimethyl terephthalate	6
Methyl halides	6
Exports	12
Others	29
Total	100

Most methanol is produced using either a high-pressure process or a lowpressure process. Almost all the methanol produced in the United States is based on the steam-reforming of natural gas. Some may be produced by using off gases from acetylene manufacture.

In the high-pressure process (above 275 bars), synthesis gas is made by reforming natural gas and forming carbon monoxide, carbon dioxide, and hydrogen. Since the reforming of methane produces an excess amount of hydrogen, it is advantageous to locate the methanol plant near an ammonia plant in order to obtain carbon dioxide to balance the excess hydrogen by the equation



This, in effect, produces more methanol. This integration is possible because carbon dioxide is removed from the synthesis gas used to make ammonia.

In the low-pressure (50 to 100 bars) methanol process, the excess hydrogen is purged from the synthesis loop and is not used to produce methanol. In this method, a larger reformer must be built in order to produce the equivalent amount of methanol.

Methanol plants are usually constructed in the size of 1000 tons/d. However, studies are being made for 5000 tons/d plants (with multiple reformers). Several plants would be located in a giant complex and could supply methanol to a fleet of tankers that would transport it from Algeria, Iran, etc. to the United States, Europe, etc. as a fuel source. This operation would be in competition with LNG transportation schemes.

Formaldehyde. Formaldehyde is consumed mostly in making urea-formaldehyde and phenol-formaldehyde resins: these resins are used in making adhesives for plywood and particle board. Also, it is used in the manufacture of acetal resin, pentaerythritol, and melamine-formaldehyde resins. Formaldehyde is made from methanol via an oxidation-dehydrogenation process in the vapor state and also by catalytic oxidation in the vapor state.

Dimethyl Terephthalate and Methyl Halides. Many processes are used to

manufacture dimethyl terephthalate by the oxidation of p-xylene, in which methanol is used to esterfy the two acid radicals. Most of the dimethyl terephthalate is used in the making of polyester fibers.

Methyl halides, that is, methyl chloride, methylene chloride, and methyl bromide, can be produced from methanol. Of the above products, methyl chloride is produced in the largest volume. Methyl chloride is made by the chlorination of methane or by the hydrochlorination of methanol; the amount being made from methanol is increasing so that only a minor amount is made from methane today. Methyl chloride is used mostly in making silicon elastomers and tetramethyl lead.

Carbon Monoxide

Carbon monoxide is used in the manufacture of acetic acid, phosgene, formic acid, and oxalic acid.

Acetic Acid. Most of the acetic acid made in the United States is from the oxidation of butane and the secondary oxidation of acetaldehyde. However, some is manufactured by reacting carbon monoxide with methanol.

Phosgene. Almost all phosgene is manufactured by the reaction between carbon monoxide and dry chlorine in the presence of activated carbon. Most phosgene is used in the manufacture of toluene diisocyanate and polymethylene polyphenylisocyanate used for the production of polyurethane resins and foams.

Formic Acid and Oxalic Acid. Both formic and oxalic acids can be made from carbon monoxide. Formic acid is made by absorbing carbon monoxide in caustic soda followed by neutralization. It is used instead of sulfuric acid in high temperature acid textile drying. Oxalic acid is made from carbon monoxide via the intermediate compound, sodium formate. It is used mostly in the pharmaceutical industry.

Oxo Alcohols

Oxo alcohols are manufactured by reacting olefins with carbon monoxide and hydrogen. In order to produce the required ratio, $1\text{H}_2:1\text{CO}$, for the oxo chemicals, the raw synthesis gas from steam reforming must be altered. For example, a low-temperature separation of the raw synthesis gas into hydrogen and a $1\text{H}_2:1\text{CO}$ mixture may be employed, or CO_2 and steam may be added to natural gas before reforming to obtain the correct H_2/CO ratio in the synthesis gas.

The short-chain-length oxo alcohols are used mostly as solvents; the intermediate chain length for plastizers for PVC, and the long-chain alcohols for detergents and lubricants.

Carbon Dioxide

Today most of the carbon dioxide used in the United States is obtained as a byproduct in the manufacture of synthesis gas for the production of ammonia, methanol, and other chemicals. The carbon dioxide is removed from the synthesis gas by an absorption process. Carbon dioxide is consumed as refrigeration in the food industry, carbonation, inerting, and as a captive raw material in the production of urea, sodium carbonate (by the Solvay process), and the manufacture of sodium bicarbonate from sodium carbonate. By far the greatest use of captive carbon dioxide is in the production of urea in which ammonia and carbon dioxide form ammonium carbamate which is dehydrated to form urea.

Methane

Figure 4 shows the products that can be made from methane as a feedstock; this, of course, excludes the chemicals that are made from synthesis gas. In general, these chemicals from methane have a much lower volume production in comparison to the products from synthesis gas. However, they are still important products.

Carbon Disulfide

Traditionally, carbon disulfide has been made by reacting charcoal with sulfur in a retort or furnace. However, all the plants built in recent years are based on the Thacker process which uses methane as the feedstock. In 1971 the manufacture of rayon and cellophane accounted for most of the United States production of carbon disulfide. The remainder of the carbon disulfide production was consumed in the manufacture of carbon tetrachloride and other chemicals.

Chlorinated Methane

Methane can be chlorinated to form methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. Depending upon the process design, one or more of these chloromethane products (or coproducts) may be produced.

Methyl chloride is produced by the chlorination of methane or by the hydrochlorination of methanol. Today, only minor amounts of methyl chloride in the United States are produced from methane. The remainder uses methanol as the feedstock.

Almost all of the methylene chloride produced in the United States is made by the chlorination of methane. Most of the methylene chloride production is used in the manufacture of paint removers, aerosol cans propellents, and solvent degreasing; i.e., its main use is as a service chemical and it has very little value as an intermediate product.

NOTE: THE NUMBER ON EACH BRANCH IS THE TOTAL PRODUCTION (THOUSAND TONS) OF THAT PRODUCT IN THE USA IN 1973. HOWEVER, NOT ALL OF THIS PRODUCTION NECESSARILY STARTED WITH NATURAL GAS AS THE FEED.

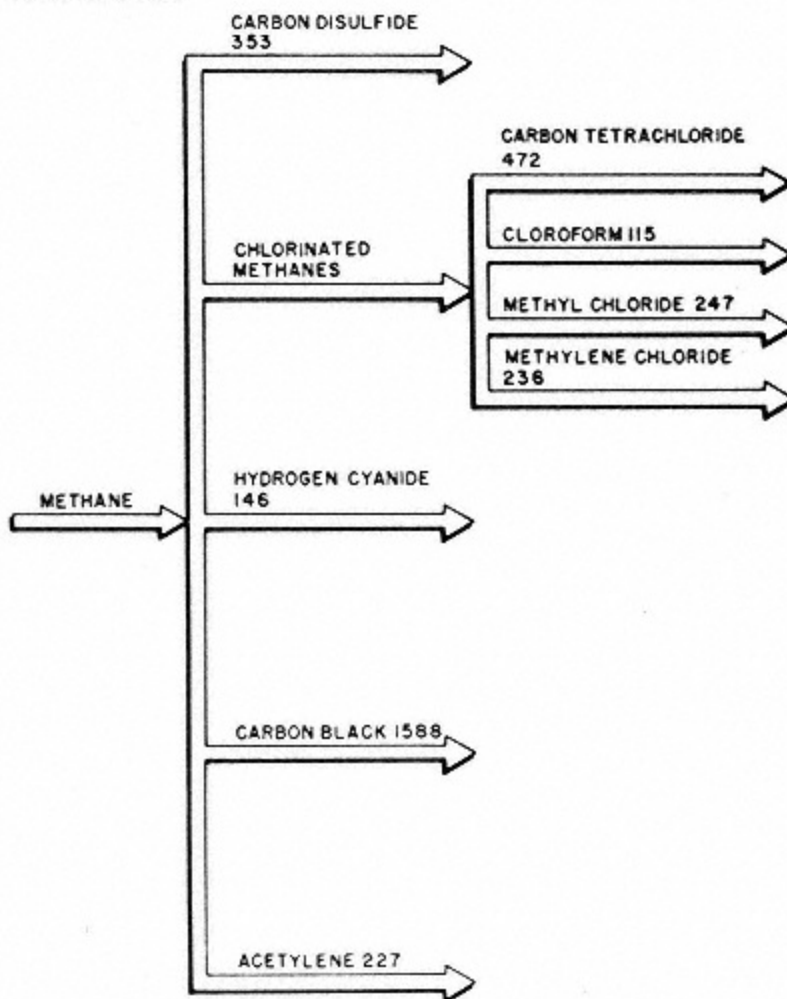


Fig. 4

Chloroform is produced by the chlorination of methane. It is used in the manufacture of fluorocarbon refrigerants, propellents, and resins.

Carbon tetrachloride is manufactured by the chlorination of methane. However, a significant amount is produced by the chlorination of carbon disulfide and as a coproduct in the manufacture of perchlorethylene from a hydrocarbon feed. Carbon tetrachloride is used in the manufacture of fluorocarbon 11 and 12 refrigerants.

Hydrogen Cyanide

Hydrogen cyanide produced in the United States is manufactured from methane, ammonia, and oxygen via the Andrusson (called Goodrich process in the United States) process. The remainder comes from the by-product recovery of hydrogen cyanide from acrylonitrile production. Hydrogen cyanide is used in the manufacture of acetone cyanohydrin, adiponitrile for nylon 66, and acrylonitrile. Today, very little hydrogen cyanide is consumed in the production of acrylonitrile because this product is now predominantly made from propylene and ammonia rather than the old route of acetylene and hydrogen cyanide. In fact, as indicated above, hydrogen cyanide is now being recovered as a by-product in acrylonitrile production.

Carbon Black

Carbon black is made from natural gas or liquid hydrocarbons, mainly by the furnace process. The natural gas or liquid hydrocarbon is partially combusted or thermally cracked. In 1955 about one-half of the carbon black manufactured in the United States used natural gas as the raw material. However, in 1973 only 7% of the total production came from natural gas with the remainder coming from liquid hydrocarbons. In 1973 the rubber industry consumed most of the carbon black production in the United States; the remainder was used in making paint and printing ink.

Acetylene

Acetylene can be produced from calcium carbide or a hydrocarbon feed. The use of acetylene as a chemical feed has decreased greatly in the last few years; the production of acetylene decreased from 453,000 tons/yr in 1970 to 226,000 tons/yr in 1974. This occurred mostly because of the switch from acetylene-based to ethylene-based processes in the production of vinyl chloride and vinyl acetate. In addition, butadiene is now being used in making neoprene, and propylene is used in making acrylonitrile.

Presently, acetylene production is used in the manufacture of vinyl chloride, acrylates, and vinyl acetate and for industrial use for welding and metal cutting. It is not expected that any new plants will be built in the United States in the near future because of its competitive disadvantages with other raw materials.

Conclusion

Natural gas is a very valuable feedstock for the chemical and fertilizer industry in that it supplies most of the feed. Also, most plants that can use natural gas or an alternate feed will be cheaper if they were based on natural gas. Thus future

plans for the allocation of natural gas must take into account its great importance as a feedstock for the petrochemical industry.

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Chemicals from Petroleum

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Introduction and Overview

In Volume 1 of his outstanding History of Chemistry [1], Partington traced the origins of chemicals by detailed analysis and convincing argument, back past the alchemists and the Greek philosophers to the Phoenicians of 1200 B.C. and beyond. But it was not until the early nineteenth century that the heavy chemicals industry proper really became firmly established as a viable entity in the rapidly growing industrial countries of Western Europe and America. As is still the case today, the large-scale production of chemicals required markets, raw materials, process plant, manpower, finance, and efficient transportation systems to succeed. These were all to be found in those nations which were already well advanced in general industrialization.

Throughout the nineteenth century the heavy chemicals industry was concerned primarily with the production of alkalis for soap, paper and glass manufacture, bleaching agents and dyes for textiles processing, and explosives for mining and military use [2].

This was also a period of concentrated research into all aspects of organic chemistry. Many new compounds were isolated for the first time and progress made on the theoretical explanation of the structure of organic substances. Two events were of particular importance to the emerging heavy chemicals industry and were to have far-reaching effects on its course of development. These were the discovery by Liebig of benzene in coal tar in 1834 [3] and the successful researches by Perkin, Caro, Graebe, Liebermann, and others on synthetic dyestuffs.

The former discovery triggered off a series of intensive studies by many famous workers into the chemical nature of the products of coal distillation. Important discoveries followed rapidly, one upon the other, so that by the time the industry was ready for synthetic dyestuffs, good supplies of relatively cheap raw materials, obtained as by-products from coal gas and coke manufacture, were already available to it. This conjunction enabled the synthetic dyestuffs section of the industry to make rapid advances at the turn of the century and led to the emergence of the heavy organic chemical industry as a distinct entity based on coal as the primary raw material.

The importance of coal as the industry's preferred source of carbon was further stimulated by the discovery in 1892 of the process for the direct production of calcium carbide from lime and coke. This gave rise to the widespread use of acetylene, first as an illuminant and later as a source of many organic chemicals by direct reaction and through the important intermediate, acetaldehyde [4].

And in 1913 the successful operation of the world's first large-scale ammonia plant using the Haber-Bosch synthesis route (with hydrogen produced by coke gasification) firmly established coal as the then preeminent raw material for the heavy chemicals industry [5].

It was during the same period, in the second half of the nineteenth century, that the petroleum industry also became firmly established. Dating for all practical purposes from 1859 the year of Drake's first well at Oil Creek in Pennsylvania the petroleum industry developed for many years quite independently of the chemicals industry. The demand for the principal products which could then be separated from petroleum, namely gasoline, kerosene, and gas oils, kept the growing industry fully occupied as suppliers of fuels.

Although the chemical nature of petroleum was already under investigation in the latter part of the nineteenth century, it is at first sight surprising that no serious plans for its use as a raw material for the chemicals industry were made until the 1920s.

There are a number of reasons for this. In the first place the most easily separated light fractions of petroleum were identified as consisting predominantly of paraffinic hydrocarbons which were recognized as being of low reactivity and therefore unsuitable for organic synthesis into the products then required.

In the second place the demands placed upon the petroleum refining section of the industry in terms of the quantity and quality of products required, enabled it to function for many years by simply separating crude oil into its several characteristic fractions using standard distillation processes. This resulted in the suppression of the development of already discovered processes for the conversion of naturally occurring petroleum hydrocarbons into the more reactive species which would have been of particular interest to the chemicals industry.

And in the third place, as already noted, the major industrialized nations were already committing themselves to coal as a basic chemical feedstock. Industrial inertia, complacency, and perhaps the fear of technological innovation restrained companies from investing in a technology which was foreign to them.

In the United States, however, the situation changed drastically in the early 1900s. The introduction of relatively cheap, mass produced motor cars increased the demand for gasoline so much that it forced refiners to explore ways in which the yield of gasoline from a given quantity of crude oil could be increased. It became apparent that a balance in refinery products could not be maintained by crude distillation alone, and that the time had come for the introduction of more sophisticated petroleum refining processes.

In 1912 William Burton successfully demonstrated the first commercial thermal cracking process which converted low valued fuel oil into higher valued gasoline. This was the first industrial application of hydrocarbon pyrolysis.

As well as solving the gasoline demand problem, the introduction of thermal cracking gave rise to a significant yield of low molecular weight olefinic gases. Initially these were burned as fuel gas or sent to the flare in the refineries. In an attempt to upgrade these potentially valuable products, the Standard Oil Company of New Jersey, in collaboration with others, developed processes for the manufacture of isopropanol, acetone, and other

derivatives from the propylene contained in thermal cracker off-gases.

So was born what today is known as the petrochemicals industry the year was 1920.

At the same time the Union Carbide Corporation, under the leadership of G. O. Curme and J. G. Davidson, was undertaking a detailed study of the possibilities of developing new process routes to heavy organic chemicals using as primary intermediates ethylene and propylene produced by the selective pyrolysis of ethane and propane. Their proposals were implemented, and by 1925 at Clendennin, near South Charleston, West Virginia, Union Carbide was producing ethylene, ethylene chlorhydrin, ethylene glycol, and ethylene dichloride on a commercial scale. Two years later ethylene oxide and glycol ethers were added to the product slate and by 1930 the world's first synthetic ethanol was produced [6].

From this point onward the petroleum-based chemicals industry progressed steadily in the United States, limited only by the development of process technology and the market demand for the products thereby made available.

The interaction between the two industries which necessarily occurred brought benefits to both parties. Thus the chemicals industry, largely used to "pots and pans" type process design, became aware of the advantages of large capacity continuous processing, for long a feature of the petroleum industry. In a similar way, the petroleum industry learned that empiricism was not essential to their operation, that a scientific approach to development and design could yield valuable results in their search for improved processes. The uniting factor was undoubtedly the science of chemical engineering, then becoming accepted as a separate discipline in its own right.

But the flow of information, ideas, and techniques across this interface caused it to become increasingly blurred. Both petroleum refining companies and chemical companies set up their separate petrochemicals organizations so that today, some 50 years later, it is difficult in many cases to define precisely where petroleum refining ceases and chemicals manufacture starts.

In Europe the development of the petrochemicals industry was not as fast as in North America. The lack of indigenous sources of crude oil, coupled with the need for strategic supplies of organic chemicals in the event of armed conflict, inhibited its growth until the early 1950s. Then with a seemingly assured supply of cheap crude oil from the Middle East, with refineries being built in all major European countries, the political conditions were judged favorable for a great surge forward into petrochemicals.

At this point it is most constructive to consider the rate of growth of the petrochemicals industry during its 50 years of existence so far. A word of caution is required, however, when petrochemicals statistics are presented for interpretation.

In the first place, unlike the petroleum industry, reliable data are hard to come by in the chemicals industry. Different researchers may have access to different sources of information, and discrepancies in quoted figures are not only likely but common.

Then there is the problem of double counting which, in this context, is meant the addition

of demand or production statistics for two or more related intermediates, say for benzene and cyclohexane. Such a figure, if combined in an assessment of "total petrochemicals," would be misleading since a large proportion of benzene is in fact utilized in the production of cyclohexane. For

TABLE 1 Ethylene Demand, 1950-1980 (millions of metric tons per year)

Year	North America	Western Europe	World
1930	0.014		0.014
1940	0.12		0.12
1950	0.64	0.03	0.67
1960	2.5	0.7	3.3
1970	7.9	5.9	18.7
1980 (predicted)	1821	1820	5464

this reason "total petrochemicals" statistics are not considered truly representative of the industry.

A more acceptable procedure is to consider the demand figures for an important primary intermediate, such as ethylene, which can be considered a general pointer to trends in the industry. Table 1 shows the relevant statistics taken from the published work of Silsby and Ockerbloom [7] and Stanley [8].

These figures indicate an average worldwide annual compound growth rate over the 30-year period 1940 to 1970 of 18% or, in other terms, the demand doubled every 5 years or so a truly remarkable sustained rate of growth. For Western Europe the growth rate over the last 20 years was even greater (approaching 30%/yr during peak periods) and most predictions indicate that the Western European annual ethylene demand should exceed that for North America by the early 1980s.

Similar statistics have been quoted for finished petrochemicals products. Table 2 lists pertinent data for three of the principal categories of end products of the petrochemicals industry derived from the published work of Balas and Jara [9].

Again, the growth rates for these products have been extraordinarily high, illustrating their general acceptance by the consumer and their production economics to be such that they can successfully compete with alternative materials.

In recent months, owing especially to the general worldwide downturn in

TABLE 2 World Production of Finished Petrochemical Products (millions of metric tons per year)

Year	Plastics	Synthetic Rubbers	Synthetic Fibers
1950	1.5	0.81	0.07
1960	7.1	1.9	0.43
1970	17.9	4.6	4.9
Equivalent average annual compound growth rate, %	16	9	24

economic activity, there has been a substantial fall in the demand for petrochemicals products. This has influenced many informed commentators to express their opinions on the possible future of the industry. As is to be expected, these opinions vary from the very pessimistic, suggesting a continued decline leading to zero or negative growth rates for the foreseeable future, to the very optimistic, suggesting that the present fall in demand is just a temporary situationsuch as has been experienced many times in the chemicals and petroleum industriesand that in the long term the market will continue to expand as before.

Most analysts would predict, however, that the future for petrochemicals lies, in all probability, somewhere between these two extremes. Certainly, higher prices will tend to suppress growth rates; at the same time, though, new uses for existing products will continue to be found and, hopefully, new products will also be introduced. As in the past, both of these effects will stimulate overall demand. The net effect is likely to be positive growth in the future but at rates somewhat lower than those experienced during the boom period of 19501970.

To those who question whether the world's unrenewable hydrocarbon resources should be utilized to manufacture synthetic materials which could well be replaced by alternatives, attention is drawn to Table 3 which compares the total energy equivalents (including raw material and conversion energies) of a representative list of basic materials. These data were published in 1974 by ICI [10].

It is readily seen that with the exception of glass and paper, the synthetic materials utilize significantly lower total energies per unit volume for their production than do their nonpetrochemical alternatives. When expressed in terms of the total energy required for finished fabricated products, the plastics rank even lower than glass and paper since, for an equivalent strength, far thinner sections are required in the case of the plastics.

TABLE 3 Total Energy Inputs of Basic Materials (kcal/cm³)

Metals	
Aluminum	158
Steel billet	82
Tin plate	102
Copper billet	112
Plastics	
Polystyrene	36
Polyvinyl chloride	28
LD polyethylene	22
HD polyethylene	24
Polypropylene	24
Others	
Glass bottles	11
Paper and board	12
Cellulose film	70

TABLE 4 Utilization of Oil and Natural Gas in OECD Countries during 1972

	Millions of Metric Tons Oil Equivalent	
Electricity generation	363.5	(13.6%)
Energy sector and losses	128.4	(4.8%)
Industry	607.7	(22.8%)
Transportation	738.0	(27.7%)
Residential/commercial	639.9	(24.0%)
Nonenergy	186.5	(7.1%)
	2664.0	100.0

Three other factors are also pertinent. First, the growth in many synthetics has not been to the detriment of nonpetrochemicals materials. This is particularly the case in fibers where the demand for cotton and wool still continues to grow (albeit slowly) and where the present demand for total fibers certainly could not now be met by existing or projected supplies of naturally occurring materials.

The second point is that there are now many examples where the properties of the synthetic petrochemically based products are so superior to the alternatives that they are virtually irreplaceable. Cable insulation, injection-molded components, detergents, and nylon hosiery all come into this category.

And the third and final point is that despite its apparent size, the petrochemicals industry still absorbs only a small fraction of the world's total hydrocarbons consumption. Table 4 presents data published by the Organization for Economic Co-operation and Development (OECD) for 1972 [11].

Table 4 shows that the nonenergy utilization of hydrocarbons in OECD countries in 1972, which includes all the raw materials used in the petrochemicals industry, was no more than 7.1% of the total. Put another way, of all the hydrocarbons consumed in 1972, 92.9% was used in energy applications (and was therefore essentially degraded to heat, water, and carbon oxides), leaving just 7.1% to be upgraded to valuable chemical products.

Perhaps the question one should really ask is: Can society afford to spend so high a proportion of its nonrenewable hydrocarbon resources on applications other than petrochemicals?

Description of Products

The question of what is or is not a petrochemical has concerned many writers on the subject. In this presentation a petrochemical is considered to be any

chemical, final product, or intermediate which is derived commercially from petroleum-based raw materials; that is, from natural gas and/or crude oil.

In most cases the petroleum-based raw material is required for its carbon content, but in others it is the actual and potential hydrogen content which appears in the final end product. Potential hydrogen is that extra hydrogen which can be derived from reacting the carbon in the hydrocarbon molecule with water. All petroleum-based synthesis gas derivatives ammonia included are petrochemicals under this definition.

The products of the petrochemicals industry may be divided into seven main categories as follows:

Plastics

Synthetic fibers

Synthetic rubbers(elastomers)

Synthetic detergents

Paints and solvents

Fertilizers

Other products

The general properties of some of the main products of these subdivisions are briefly described under separate headings below.

Some 80% of the petrochemicals industry's organic chemicals output is produced in the form of synthetic polymers which are most widely used for plastics, synthetic fibers, synthetic rubbers, and paints.

Polymers are high molecular weight materials consisting of long-chain molecules, which are built up of smaller molecules linked together by strong, attractive forces. Some polymers occur naturally, others are synthesized from component small molecule materials or monomers.

Two distinctly separate types of polymers may be identified: thermoplastic polymers which can be repeatedly softened on heating and thermosetting polymers which cannot. Thermosetting polymers consist of rigid molecular structures which make them brittle and unsuitable for synthetic rubbers and fibers; they are, however, suitable for certain plastics applications. In contrast, thermoplastic polymers may be used for many purposes depending upon the physical properties of the finished material.

Plastics

Three thermoplastics, polyethylene, polyvinyl chloride, and polystyrene, and one group of thermosetting plastics, the formaldehyde resins, dominate the world plastics market.

Other plastics, including polyurethane, the acrylonitrile-butadiene-styrene copolymers (ABS resins), polypropylene, and polyester resins, are produced in intermediate quantities, while the remainder are made on a much smaller scale for very specialized markets.

Polyethylene is produced in two forms: low-density polyethylene (LDPE), which was first developed in the 1930s, and high-density polyethylene (HDPE), a slightly more expensive, more highly crystalline version developed later.

LDPE is produced by polymerizing ethylene at high pressure in the presence of traces of oxygen. LDPE is partially crystalline and is almost transparent, which makes it suitable for its biggest outlet, transparent wrapping sheet. Significant quantities are also used for injection moldings (bowls, buckets, etc.), pipes, and insulating coatings. HDPE is produced at about atmospheric pressure by bubbling ethylene through a catalyst suspended in an organic liquid. In contrast to LDPE, HDPE is almost completely crystalline and opaque. It has a higher tensile strength, more rigidity, and a higher softening temperature than LDPE: it is also resistant to hot water and solvents. Its main use is for thin-walled containers, which can be made by blow molding.

Polypropylene (PP) is produced in a similar way to HDPE and it has a similar crystalline structure. It is a better plastic than HDPE in a number of ways: lower density, higher tensile strength, greater rigidity, and higher melting point. It is also resistant to chemical attack and to abrasion. These superior properties make PP competitive with HDPE in a number of film and molding services.

Polyvinyl chloride (PVC) is produced from the monomer, vinyl chloride, by a number of alternative processes. It is a slightly crystalline polymer and is almost opaque. PVC can be produced in many forms, ranging from rigid to pliable, by the addition of different quantities of plasticizer material which when added to a polymer softens it. PVC has been found to be more suitable than any other polymer for use with plasticizers, and so about 90% of all plasticizers are used in PVC processing. Esters of phthalic acid are the most widely used of many different types of plasticizer. Plasticized PVC is used for sheet, fabric coating, floor coverings, cable insulation, hosepipes, shoes, and boots. Rigid PVC is used for piping, ductwork, gramophone records, bottles, and sheet.

Polystyrene, produced from the monomer styrene, has low crystallinity, is transparent, and is somewhat brittle. Its particular advantages are its ease of molding, dimensional stability, and freedom from odor, taste, and toxicity. Its great disadvantage is that it is degraded by ultraviolet light and so cannot be used for outdoor applications.

Polystyrene is suitable for producing transparent film or sheet, the brittleness being reduced by stretching. Its main outlets are as moldings (vending cups, food containers, refrigerator internals, electrical insulation, flower pots, etc.) and as polystyrene foam (packaging, thermal insulation, etc.).

To increase its impact resistance, 3 to 10% of styrene-butadiene rubber (SBR) or polybutadiene may be included in the polystyrene formulation. High impact polystyrene produced in this way is rapidly superseding general purpose polystyrene, particularly in molding applications.

The acrylonitrile-butadiene-styrene (ABS) copolymers are similar in many respects to high impact polystyrene, both having discrete rubber particles dispersed in a thermoplastic polymer phase. The recipe for ABS resins usually requires approximately 50% styrene, 25% butadiene, and 25% acrylonitrile.

There are a number of different ways of producing ABS resins and many types of product. They are characterized by their high heat resistance, high tensile strength, and good general engineering properties.

ABS resins are used widely in the automotive industry and for high quality

precision moldings (such as telephones, calculator housings, etc.). It is also possible to chromium plate ABS, and in this form it is able to replace chromium-plated metal parts in some applications.

The most important group of thermosetting plastics are the formaldehyde resins. The phenol formaldehyde (PF) resins were discovered in the nineteenth century and developed in the 1920s under the trade name Bakelite. The onestage resins are made by polymerizing phenol and formaldehyde in the presence of an alkaline catalyst directly to the thermosetting plastic. They are used for high impact moldings and with cloth or paper to produce laminates.

The two-stage resins are first polymerized with an acid catalyst to give an intermediate thermoplastics polymer. This is used as a general-purpose molding material and may be mixed with up to 85% of an inert filler which can be sawdust, stone, asbestos, mica, etc. The second stage of the polymerization to the finished thermosetting plastic is carried out in the mold with the addition of formaldehyde and heat.

The great attraction of PF resins is that they are the cheapest of all molding materials since the finished article can contain such a high proportion of inert filler. PF resins, however, cannot be colored and they possess poor mechanical properties. They are used for general purpose, low impact moldings, as bonding agents (grinding wheels and brake linings), and as binders for chipboard and similar products. An important application for PF resins is in exterior or marine grade plywood where they provide the necessary water resistance.

The world production of PF resins is still increasing slightly though at nothing like the rate of the three main thermoplastics.

The urea formaldehyde (UF) resins are about as important as the PF resins. They are not as resistant to water as the PF resins, but are almost colorless and stable to light.

UF resins are used for molding powders, as binders for chipboard and similar products, and for interior-grade plywood. They are also used to creaseproof cotton fabrics and to impart wet strength to paper goods.

Melamine formaldehyde (MF) resins are produced on a smaller scale. They are colorless, stable to light, and resistant to water. They find wide application in high quality laminates and for tableware.

Polyester resins are produced by the reaction of ethylene or propylene glycol with maleic anhydride or phthalic anhydride. They are viscous liquids which are cured by cross-linking with styrene in the presence of a catalyst. Polyester resins are mainly used with a fiberglass filler in the construction of boat hulls, car bodies, etc. They have the advantage over the formaldehyde resins in that they can be cured without the application of heat and no water is driven off during the process. They are, however, very much more

expensive than the formaldehyde resins.

Polyurethanes are produced by reacting diisocyanates with suitable polyhydroxy compounds; tolylene diisocyanate and polypropylene glycol are the usual reactants. Polyurethanes are produced in four distinct forms; namely rigid foams (used in construction, roofs, walls, etc.), flexible foams (furniture, bedding, buoyancy aids, etc.), elastomers (industrial tires, foundation garments), and surface coatings.

Fibers

Fibers are materials which are much stronger along their length than across it. They are polymers with long straight chain molecules lying side by side, held together by entanglement forces. Most fibers exhibit some degree of crystallinity which improves the synthetic fibers' strength and is usually increased during processing by stretching at temperatures above the softening point of the noncrystalline material. Fibers must be thermoplastic polymers but the polymer molecules must not have long bulky branch chains, since these interfere with the drawing operation and prevent ordered alignment. Fibers fall into four distinct categories: two occur naturally, a third is semisynthetic, and the fourth is wholly synthetic.

The two naturally occurring groups are vegetable and animal fiber. Cotton, the principal vegetable fiber, still holds the number one position in the world market and is about the cheapest of the quality fibers. Wool, the main animal fiber, accounts for a much smaller percentage of the world market and is at the top of the fiber price range.

Rayon, the most important, nonpetrochemical semisynthetic fiber, was introduced in the 1920s and rapidly gained a large share of the world market as a substitute for cotton at a competitive price. Rayon is produced by chemically dissolving naturally occurring cellulose, typically wood pulp, and regenerating the cellulose polymer as a continuous filament. Rayon is a cheap, versatile fiber which is still produced in larger quantities than any single synthetic fiber. It can compete in both the low cost and the higher quality markets and is finding increasing application as a cotton substitute for blending with synthetic fibers.

The fourth category of fibers are those that are truly synthetic and produced today from petrochemicals intermediates. Nylon was first produced in the 1930s and polyester fiber in the 1940s but both had to await major advances in technology before their basic raw material could be produced cheaply enough for their competitive introduction to the market.

Currently, over 90% of the world fiber market is held by 6 fibers: cotton 47%, viscose rayon 14%, nylon 10%, polyester 9%, wool 7%, and acrylics 5%. Production of the natural fibers, cotton and wool, is almost static, rayon output is still increasing but not as fast as the synthetics nylon, polyester, and acrylics.

Nylon is a generic term which applies to a family of polymers the polyamides. Two members of this family are produced on a large scale, and these are known respectively as nylon 66 and nylon 6.

Nylon 66 is the polymerized salt of adipic acid and hexamethylene diamine and is the earlier product, predominating in the United States and the United Kingdom.

Nylon 6 is polymerized caprolactam. It has similar properties to nylon 66 but possesses

better abrasion resistance hence its preferred use when this property is important, e.g., automotive upholstery and seat belts.

Since the introduction of polyester fibers, nylon has been steadily replaced as a synthetic fiber for clothing; its use in hosiery, however, is still unsurpassed. The nylons are still used widely for domestic and industrial fabrics, carpeting,

etc. In the United States they also find application for reinforcing in tires although rayon is far more commonly used for this purpose in other countries.

Polyester refers almost exclusively to polyethylene terephthalate. It is made by the condensation of ethylene glycol with terephthalic acid. Polyester does not absorb water and does not shrink. It has to be heated to about 150°C during drawing to increase crystallinity, consequently any creases put into fabrics at these temperatures will remain in place at ordinary temperatures and the garment will not become creased during normal washing. Polyester is usually blended with cotton, wool, or rayon to produce a tough, crease-resistant, moisture-absorbent, soft-textured fabric. Polyester is largely replacing nylon as the preferred synthetic fiber for clothing.

Polyester is a very versatile fiber finding increasing applications in many fields including fabrics, tires, carpets, and hosepipes. It is the fastest growing synthetic fiber at the present time.

Acrylic fibers are usually made from the polymer of acrylonitrile. Polymerization takes place in water and the fibers are spun from solution, since polyacrylonitrile decomposes before melting. Acrylic fiber competes mainly with wool where its lower price has provided it with an expanding market in knitted goods. It is also utilized in carpeting.

Synthetic Rubbers

Rubbers or elastomers are materials which stretch easily and return to their original shape when the stress is removed. Synthetic rubbers are produced from thermoplastic polymers which in their initial state can easily be permanently deformed. The elastomer is produced by loosely fixing the molecular chains relative to each other by linking them with sulfur atoms; this is the process of vulcanization. Synthetic rubbers are vulcanized by similar methods to natural rubbers, soft rubbers requiring about 4% sulfur. As more sulfur is added, the rigidity of the rubber increases until it becomes a hard cross-linked thermoset plastic.

The essential component in natural rubber is polyisoprene, which is the liquid (latex) obtained from rubber trees. Although isoprene was first synthetically polymerized in the nineteenth century, the product was far inferior to natural rubber. Technological advances since then, however, have been such that the structure of natural rubber can now be so closely reproduced that synthetic polyisoprene can be used for almost all applications which would otherwise require natural rubber. Polyisoprene has been shown to be superior to alternative synthetic rubbers in certain special applications such as in heavy duty and aircraft tires.

Butadiene is by far the most important chemical in the synthetic rubber industry. About 60% of the world market is held by styrene-butadiene rubber (SBR), which is based on a copolymer of about 75% butadiene and 25% styrene. Polybutadiene rubber (BR) itself holds almost 20% of the market.

Butyl rubber, a copolymer of isobutylene and isoprene (3%), is the next most important rubber. It is an extremely stable synthetic rubber used for conveyor belts and tire inner tubes but it appears to be decreasing in importance as other, cheaper products are introduced.

The nitrile rubbers are copolymers of butadiene and acrylonitrile. They have good chemical and oil resistance and are used in applications where these properties are particularly important such as fuel hoses and printing rolls.

Synthetic Detergents

A detergent is used with water to remove dirt from the surface of an article and to hold it in the water as an emulsion and so prevent redeposition on the surface.

Detergent molecules are long, though not as long as those of polymers. A necessary feature is that the two ends of the detergent molecule are chemically different; one end is a hydrocarbon and therefore hydrophobic (water repellent), while the other end is an inorganic salt of sodium or potassium, which is hydrophilic (water soluble).

When dirt molecules are loosened from the surface the detergent molecules surround them with the hydrophobic end toward the dirt and the hydrophilic ends facing outward to the water. The dirt particles are thereby held as an emulsion in the water and cannot redeposit on the article.

Soaps are sodium salts of straight chain organic acids made from natural fats and oils. These are good detergents and are biodegradable, that is, they can be broken down by bacteria, but they form insoluble calcium and magnesium salts which reduce their efficiency in hard waters. Their main disadvantage is the cost and limited supply of the natural oils required to produce them. Synthetic detergents have therefore filled the increasing market for cleansing materials.

The most important class of synthetic detergents are the sodium salts of sulfonic acids. The sulfonic acid is produced by reacting benzene with a high molecular weight olefin and sulfonating with sulfur trioxide. Originally, the olefins were produced by polymerizing propylene; however, this produced branched chain molecules which were not biodegradable. Detergents in liquid effluents accumulated in rivers and built up to toxic levels; they also produced stable foams which floated on the rivers.

It was found that when straight chain olefins were reacted with benzene and sulfur trioxide, biodegradable detergents could be produced. Most developed countries have now changed to these. Such detergents are termed linear alkylbenzene sulfonates. Another group of biodegradable detergents is made by condensing ethylene oxide with higher alcohols and phenols. These are called nonionic detergents, are low foamers, and are used extensively in industry and for household liquid detergents.

Paints and Solvents

A paint must be easy to apply and it must adhere to the surface in a homogenous layer. It should be opaque and its color should not change with age. The paint must protect the surface to which it is applied and it should therefore be resistant to abrasion and corrosion. It is often an advantage if the paint dries quickly.

The three main components of a paint are the pigment, the binder, and the solvent. The pigment provides the color and most of the protective layer.

Titanium dioxide is the most widely used pigment today, with other pigments being added in smaller quantities to give the required colors. The binder holds the pigment together in a homogenous layer. In traditional paints the binder was linseed oil with natural resins (shellac or rosin) added to produce a harder surface.

The availability of synthetic polymers has provided new binders and made water-based emulsion paints possible. The oil-modified alkyd resins have largely replaced the linseed oil-shellac binders. As a result, modern oil paints are quicker drying, they produce harder finishes, and are more durable.

Turpentine, the traditional solvent, has now given way almost completely to white spirit, a light, highly refined petroleum fraction.

A solvent is necessary to reduce the initial viscosity of the paint so that it may be applied easily, but it is lost on evaporation as the paint dries.

The introduction of water-based emulsion paints stemmed from the desire to eliminate the solvent and so lower the cost of the paint. Polyvinyl acetate and polymers of acrylonitrile or acrylic esters are the binders of the water-based emulsions. These give rise, respectively, to the "vinyl" and "acrylic" water-based emulsion paints. The emulsion paints are quick drying and odorless. They are mainly used for interior decoration, though recently improved products have been developed for outside application.

In addition to white spirit, a wide range of special solvents is also produced from petroleum sources. These find applications in the surface coating, pharmaceuticals, textiles, and the photographic industries among others. Some are essential for metal degreasing and dry cleaning while others are used extensively in the petrochemicals industry itself.

Fertilizers

The need to put back into the soil nutrients which have been depleted by constant crop harvesting has been known for over 2000 years. Until relatively recent times, "natural" or "organic" fertilizers were most commonly utilized, animal manure being the principal material, supplemented by bone meal and wood ash.

In the nineteenth century, when the elements of plant chemistry were starting to be understood, it was recognized that soil fertility could be maintained by "inorganic" fertilizers. Ammonium sulfate derived from the same coal carbonization process which provided the emerging organic chemicals industry with its first raw materials rapidly became established as a leading nitrogenous fertilizer along with naturally occurring saltpeter (potassium nitrate).

The successful development of the Haber-Bosch ammonia synthesis process in the early 1900s enabled atmospheric nitrogen to be "fixed," commercially, for the first time. With synthesis gas derived from coke, this formed the original basis of the nitrogen sector of

the heavy chemicals industry. In more recent years, large-scale petroleum-based synthesis gas processes have become available and the whole situation has undergone dramatic changes.

Today the petrochemicals industry is responsible for almost all of the world

ammonia production, by far the greatest proportion of which (approximately 80%) is used for fertilizers in the form of anhydrous ammonia, ammonium nitrate, ammonium sulfate, ammonium phosphate, urea, and compound NPK fertilizers.

The world demand for ammonia has been steadily increasing (at about 8% per year) as both developed and developing countries seek to improve farm crop yields. The 1975 world nitrogen demand is estimated at 42,000,000 t which makes ammonia the largest tonnage single chemical product of the whole petrochemicals industry [12].

Other Products

There are many petrochemical products which do not fall into any of the six categories defined above. Generally speaking, they are produced on a substantially smaller scale although it must be recognized that technological advances in almost any section of the petrochemicals industry could bring about rapid changes in the demand of individual chemicals. Thus today's "other product" could well be tomorrow's "wonder product."

Included under the "other products" heading are pharmaceuticals (hypnotics, tranquilizers, antidepressants, antihistamines, sulfonamides all produced synthetically from petrochemical raw materials); dyes; insecticides, herbicides, fungicides, and other agrochemicals; bleaches (hydrogen peroxide and related compounds); plasticizers; and food additives.

Another group of products are made directly from petroleum fractions without passing through complex intermediate stages. These include elemental sulfur, carbon black, naphthenic acids, and last but by no means least, synthetic protein for animal and possibly, in the future, human consumption.

Primary Intermediates

In the previous section the general properties of the seven main categories of end products of the petrochemicals industry were summarized by reference to some of the more commercially important chemical species. The total output of the industry is, however, vast and many thousands of products, too numerous to list here, are produced from an immense range of chemical formulations and recipes.

The starting point for all these products is crude oil and/or natural gas. Many processing stages are required to convert the oil or gas into the simplest finished product. The chemicals emerging from the intermediate stages of processing are known as "intermediates." They are petrochemicals in their own right, produced to high standards of purity and are freely marketable between companies and countries.

This section deals with the production of the "primary intermediates"; that is, the large-scale production of the first rank of petrochemicals intermediates from their petroleum raw materials.

The primary intermediates, sometimes referred to as the "basic building blocks" of the petrochemicals industry, are low molecular weight, reactive chemicals, the most important of which may be classified in three main categories. These are as follows:

Olefins notably ethylene, propylene, butadiene, and the butylenes

Aromatics notably benzene, toluene, and the xylenes

Synthesis gas hydrogen and carbon monoxide

In earlier times other primary intermediates (and acetylene in particular) have held positions of importance in the petrochemicals industry, but these have since declined and are not considered here.

The way in which the three main types of primary intermediates are produced are discussed under separate headings below. In a later section their utilization in the production of secondary and higher order intermediates, leading to finished products, will be discussed.

Olefins

Olefins are produced from petroleum fractions by the process of pyrolysis or thermal decomposition. Though now highly developed, the process has a long history dating back to the work of Henry who in 1805 reported the results of his experiment on the pyrolysis of animal oils, fats, and waxes and noted for the first time the formation of ethylene therefrom [13].

In hydrocarbon pyrolysis, the petroleum fraction is heated rapidly in the presence of steam to a high temperature under which conditions it undergoes molecular decomposition, thereby producing a mixture of lower molecular weight hydrocarbon species. Under the right conditions of temperature, pressure, and residence time, the pyrolysis process can be made selective and aimed toward the preferential production of olefins particularly ethylene, propylene, butadiene, and the butylenes.

Although a number of widely different pyrolysis reactor types have, in the past, been proposed, the externally heated, continuous flow tubular reaction system is, today, pre-eminent in the field.

In this system the hydrocarbon feedstock is first vaporized, mixed with steam, and then passed through a tube located in the firebox of a specially designed furnace. Since the desired end products are those that are predominantly produced by fast primary pyrolysis reactions, the residence time is kept short (typically 0.1 to 0.5 sec) so as to suppress the slower secondary reactions which give rise to the formation of unwanted tars and polymers. High temperatures and low pressures favor the production of olefins, and optimum reactor outlet conditions for most hydrocarbon feedstocks are generally found to be in the range of 800 to 900°C at 1.4 to 2.0 bars pressure.

Figure 1 shows the layout of a typical hydrocarbon pyrolysis furnace. In this particular design the reaction tube is divided into three separately heated zones so as to give control over the temperature profile within the reactor.

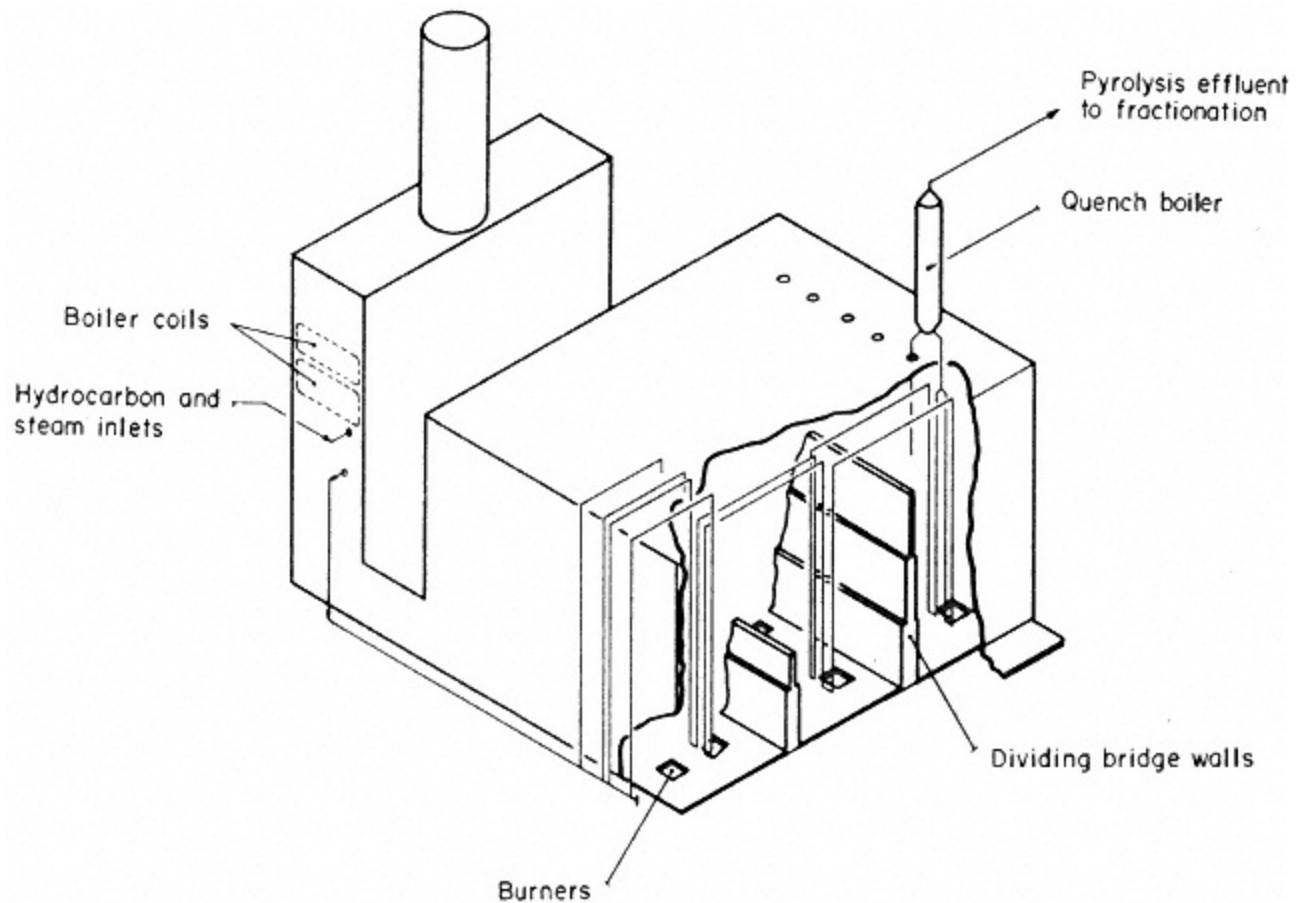


Fig. 1.
Typical three-zone hydrocarbon pyrolysis furnace.

Emerging from the pyrolysis furnace, the pyrolysis products are rapidly quenched to arrest the reaction processes and so afford precise control over the residence time/temperature history within the total reaction system.

Figure 2 shows a block flow diagram of a complete olefins plant based on a petroleum naphtha or gas oil feedstock.

The quenched pyrolysis gases are first fed to a primary fractionation system for the recovery of heavier hydrocarbons in the gasoline, gas oil, and fuel oil boiling ranges. The overhead vapors are compressed, additional gasoline being recovered from the interstage cooler condensates. The compressed gas is then washed to remove acid gases and dried before entering a low-temperature chilling train leading to the demethanizer. Product hydrogen and methane are recovered from this section of the plant.

The demethanizer bottoms are then fractionated into the required olefin products by five further towers, namely the deethanizer, depropanizer, debutanizer, and the C₂- and C₃-splitters. Acetylene, methyl acetylene, and propadiene are reduced to acceptable levels by selective hydrogenation in reactors placed immediately upstream of the C₂- and C₃-splitter towers.

Typical yields of light olefins obtained by the pyrolysis of various hydrocarbon feedstocks have recently been tabulated by Zdonik et al. [14]. Pertinent data are listed in Tables 5

and 6.

The selectivity toward ethylene is clearly seen from these tables; high yields of this important primary intermediate being obtainable from a wide range of petroleum feedstocks with the exception of i-butane.

The steam pyrolysis of i-butane is a special case Very little ethylene is produced but the yield of isobutylene is significant. When isobutylene is

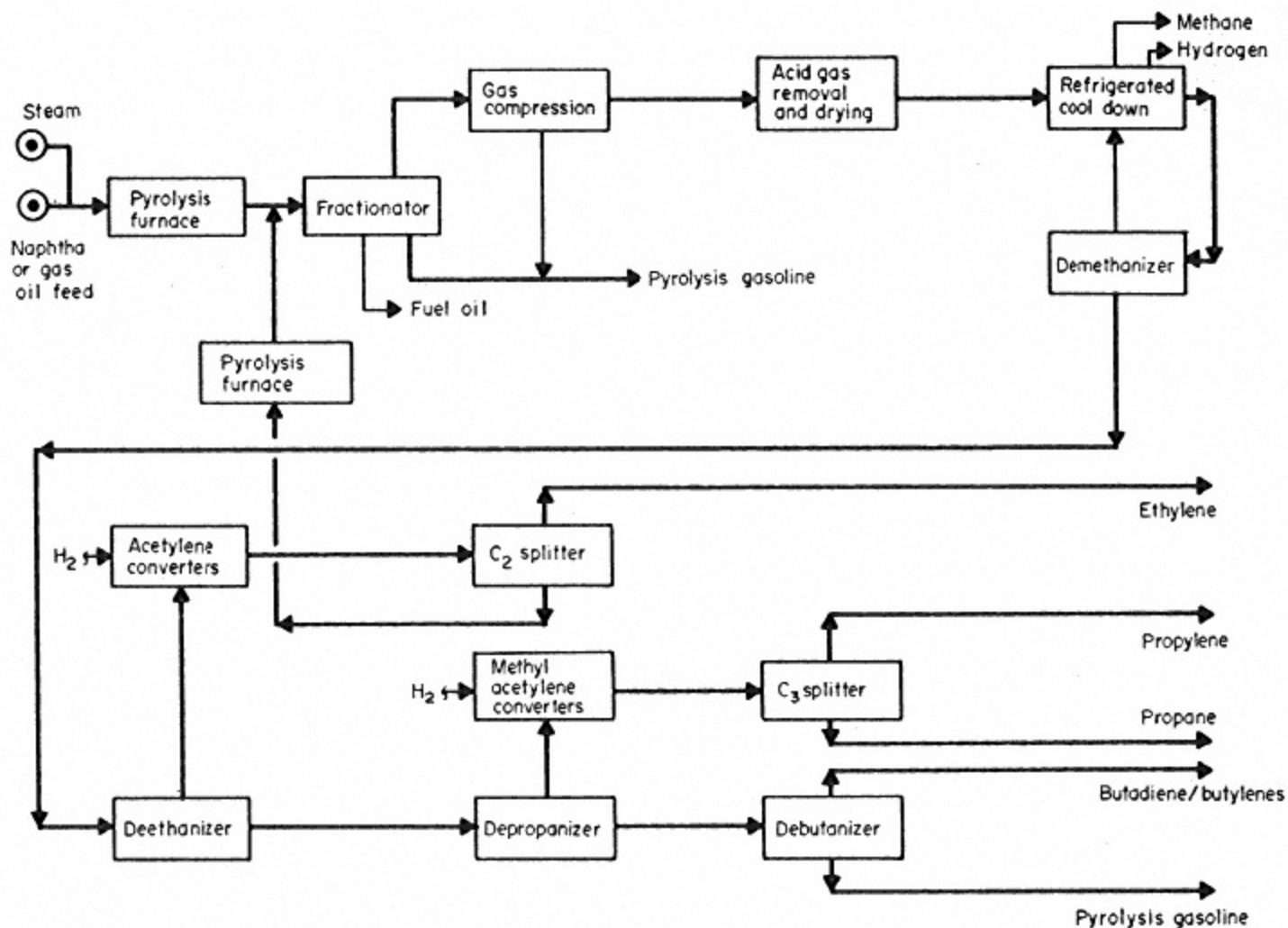


Fig. 2.

Typical block flow diagram for olefins production.

extracted from the C₄ product for further use, the i-butane may be recycled to pyrolysis giving an ultimate yield of isobutylene on fresh i-butane feed approaching 50%.

It is also apparent from Table 6 that in liquid hydrocarbon pyrolysis, the severity required to maximize the yield of one valuable product does not necessarily correspond to that required for another. Thus over the range covered, a high pyrolysis severity, while favoring ethylene production, depresses the yield of the other light olefins.

This point is better illustrated in Fig. 3 where the relative yields of ethylene,

TABLE 5 Pyrolysis of Light Hydrocarbons

Feedstock	Ethane	Propane	n-Butane	i-Butane
Conversion, %	60	92	96	51
Yield, mol%				
Ethylene	33.8	30.0	28.5	2.7
Propylene	1.0	7.6	10.8	12.8
Butadiene			0.8	
Butylenes	0.4	1.2	1.1	14.0
Butanes			1.8	30.9

TABLE 6 Pyrolysis of Liquid Hydrocarbons

Boiling range, C	Feedstock			
	Kuwait Naphtha 30170		Kuwait Gas Oil 230325	
	Low	High	Low	High
Ethylene	25.8	31.3	19.5	26.0
Propylene	16.0	12.1	14.0	9.0
Butadiene	4.5	4.2	4.5	4.2
Butylenes	7.9	2.8	6.4	2.0

propylene, and butadiene are plotted against relative pyrolysis severity. This plot is derived from the published work of Chambers et al. [15] and is typical for normal liquid hydrocarbon pyrolysis; the maximum yields of different product species occur at different pyrolysis severities. It is for this reason that at an olefins plant the pyrolysis furnace operating conditions are best set to give the optimum overall yield spectrum of products, and this may not necessarily coincide with the maximum yield of any one product. Furthermore, the optimum yield spectrum is strongly dependent upon product values (or transfer prices between plants), and these can vary from day to day depending upon factors quite outside the control of the plant manager.

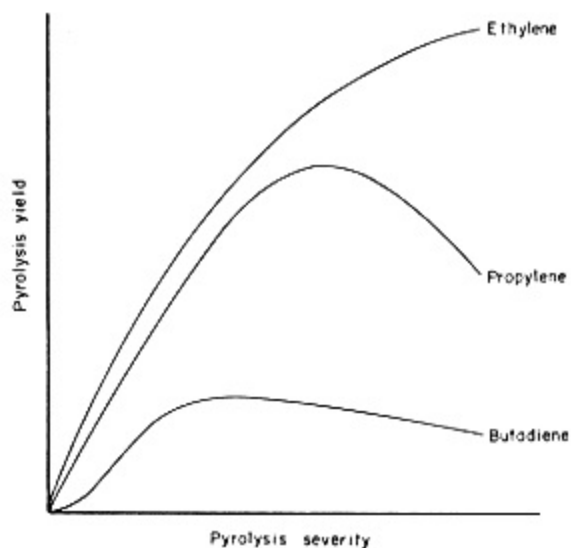


Fig. 3.
Effect of pyrolysis severity on yields [15].

While the ethylene and propylene products of pyrolysis are produced directly from an olefins plant in a high degree of purity, ready for polymerization or conversion to secondary intermediates, the butadiene is not.

The butadiene is contained in a mixed C₄-stream along with a broad spectrum of light hydrocarbons of similar boiling point. Table 7 shows a typical composition of such a C₄ fraction derived from naphtha pyrolysis, in order of increasing boiling point [16].

Because of the closeness of the boiling points, it is not practicable to separate out the butadiene by fractional distillation.

Two quite different types of processes are employed on the commercial scale.

The first employs liquid-phase extraction with a selective solvent such as cuprous ammonium acetate (CAA). The solvent extraction is carried out in a series of countercurrent stages, butadiene is desorbed from solution and distilled to remove traces of ammonia, water, and any polymer formed during processing.

The second type of process, now preferred, is extractive distillation. Relative volatility modifiers such as acetonitrile, furfural, dimethylformamide, dimethylacetamide and n-methylpyrrolidone are all employed in proprietary commercial processes. For polymerization grade butadiene some of these processes require the C₄ feedstock to be pretreated to reduce its acetylenic hydrocarbon content, others do not.

Isobutylene may be separated from the butadiene free C₄-stream by its selective absorption in sulfuric acid and subsequent desorption.

TABLE 7 Typical Composition of C₄ Fraction from Naphtha Pyrolysis

	Wt. %
Propylene	0.4
Propane	0.5
Propadiene (allene)	0.1
Propyne (methyl acetylene)	0.3
i-Butane	1.0
Methyl propene (isobutylene)	26.5
Butene-1	16.9
Butadiene-1,3	40.0
n-Butane	3.0
trans-Butene-2	6.0
cis-Butene-2	4.8
Butenyne (vinyl acetylene)	0.25
Butyne-1 (ethyl acetylene)	0.1
Butadiene-1,2	0.1
Butyne-2 (dimethyl acetylene)	0.05
	100.00

In addition to producing light olefins, hydrocarbon pyrolysis also yields a gasoline fraction rich in aromatics when petroleum naphtha or gas oil are the chosen feedstocks. The aromatics are frequently extracted from the pyrolysis gasoline and used to supplement aromatics produced from other sources. In this way an olefins plant sized for 500,000 t/yr of ethylene may also produce over 100,000 t/yr of benzene together with 50,000 t/yr of toluene and 30,000 t/yr of xylenes.

Steam pyrolysis is today the principal source of the olefinic primary intermediates. Other sources do exist; thus ethylene, propylene, and butylenes are sometimes recovered from refinery fluid catalytic cracking operations. In North America, butadiene is produced in substantial quantities by the catalytic dehydrogenation of n-butane and the butenes.

But at the center of most large, integrated petrochemicals complexes is situated an olefins plant the first step in converting a petroleum raw material into a wide range of finished petrochemical products.

Aromatics

Although, as previously stated, significant quantities of aromatics may be recovered from the pyrolysis gasoline product of an olefins plant, the most important process for their large-scale production is catalytic reforming. Thus in the United States about 80% of all aromatics are so derived; in Western Europe the figure is closer to 60%, reflecting its greater dependence on naphtha and gas oils for olefins production [17].

The catalytic reforming process was originally introduced in the early 1950s for the purpose of increasing the octane rating of the petroleum refinery gasoline pool.

The feed to a catalytic reformer is normally a petroleum distillate fraction, broadly speaking of the same boiling range as the desired reformate product. The octane rating enhancement of gasoline blendstocks in catalytic reforming results from a combination of a number of simultaneous reactions, the most important being the dehydrogenation of naphthenes to aromatics, the dehydrocyclization of paraffins to aromatics, and isomerization. The net effect is the conversion of naphthenes and normal paraffins to aromatics and isoparaffins.

The reforming reactions take place at elevated temperature and pressure in an atmosphere of hydrogen over a precious metal catalyst. Many catalyst types and formulations have been used in catalytic reforming, but today, although the technology is still evolving, the bifunctional platinum on alumina combination, with or without various promoters, etc., remains the basis of essentially all commercial processes.

Figure 4 shows a simplified flow sheet of a typical catalytic reformer. The feedstock, which may be a virgin naphtha or a distillate fraction derived from another process such as fluid catalytic cracking or hydrocracking, is first fractionated to remove light hydrocarbons which will not benefit from catalytic reforming (pentanes and lighter). The

fractionated feedstock is then hydrotreated to reduce the sulfur and nitrogen contents to acceptably low levels as these act as poisons to the reforming catalyst.

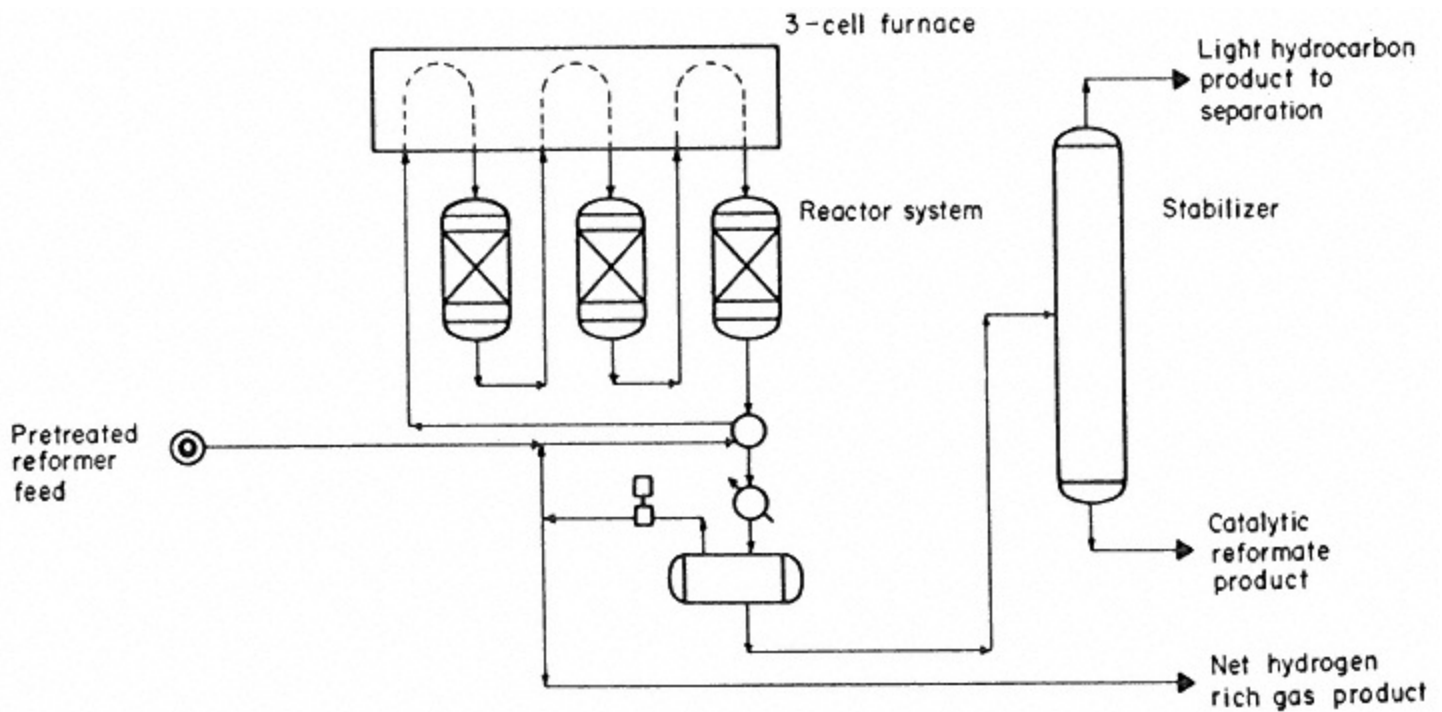


Fig. 4.
Simplified flow sheet of typical fixed bed catalytic reformer.

The pretreated feedstock is preheated, mixed with the hydrogen-rich recycle gas stream, and passed to the reaction system. This consists typically of three (or sometimes four) fixed bed reactors in series with reheat between the stages to provide the endothermic overall heat of reaction and to maintain the optimum temperature profile in the system. Typical reaction conditions are 480 to 540°C and 20 to 30 bars pressure with older catalysts but at substantially lower pressures, down to 7 bars, with the newer bimetallic catalysts [18].

The reactor effluent is cooled, the hydrogen-rich gas separated for recycling and for use in other processes, and the liquid-phase fractionated to give product reformate and light hydrocarbons for recovery as required. The research octane number of the reformate is typically of the order of 100 (clear), and this can be produced from a feedstock having an octane number as low as 50.

There are many alternative types of reactor designs now available. Most are of the fixed bed type requiring catalyst reactivation at relatively infrequent periods (about twice annually), but some newer designs incorporate moving catalyst beds with continuous reactivation.

Much of the octane improvement in catalytic reforming is due to the formation of aromatics, particularly toluene and the xylenes. At very high reforming severity the reformate may contain up to 77% total aromatics. High severity, however, is accompanied by a loss of reformate yield on feed and also a loss of nonaromatics in the gasoline boiling range which could be of value elsewhere in the complex. This effect is illustrated in Table 8 from published data of Mager [19].

Despite the significantly higher loss of hydrocarbon to fuel gas, butanes, etc., the trend when reforming for aromatics is toward high operating severity. This is because the savings in the cost of the catalytic reformer and associated aromatics recovery plant outweigh the value of the downgraded hydrocarbon.

A typical componential breakdown of the aromatics obtainable from a catalytic reformer designed for aromatics production is listed in Table 9 [20].

TABLE 8 Aromatics Yield as a Function of Severity

Reformer severity Research Order Number clear, %	8991	9395	99100
Yields, vol % on feed			
Aromatics	41	44	47.5
Nonaromatics	44	36	24.5
Total reformat	85	80	72
Fuel gas, butanes, etc.	15	20	28
Aromatics vol.% on reformat	48	55	66

The C8-aromatics fraction consists of the three isomers of xylene and ethylbenzene approximately as shown in Table 10 [19].

The separation of aromatics from catalytic reformat and their subsequent purification for petrochemicals use presents a difficult process design problem for which there are many commercially proven solutions. The first stage generally makes use of solvent extraction to separate aromatics from nonaromatics. Several different solvents have been proposed and utilized for this service including anhydrous sulfur dioxide (now obsolete), glycols, n-methylpyrrolidone (NMP), sulfolane, dimethylsulfoxide, and morpholine.

Following extraction the aromatics are purified by conventional fraction-

TABLE 9 Typical Analysis of Aromatics in Catalytic Reformat

Severity, Research Order	100
Number clear, %	
Yields, wt. % on total aromatics	
Benzene	9
Toluene	33
C8-aromatics	41
C9-aromatics	17
	100

TABLE 10 Analysis of C8-Aromatics in Catalytic Reformat

	Typical %	Range %
o-Xylene	23	1926
m-Xylene	40	3540
p-Xylene	17	1620
Ethylbenzene	20	1721

ation to yield high-purity benzene, toluene, and C₈-aromatics fractions. These, strictly, are the primary intermediates, but in a large proportion of actual installations further processing stages are added in order to give a measure of control over the relative yields of the required aromatics. Thus a particular complex may have no use for toluene but a high demand for benzene. Also, as noted from Table 10, the C₈-aromatics fraction contains a large proportion of m-xylene for which there is normally a low demand in the petrochemicals industry.

A typical arrangement of an integrated aromatics production facility is illustrated in Fig. 5. This shows a catalytic reformer, aromatics extraction, and fractionation process train as outlined above. In addition, a hydrodealkylation plant is included to convert excess toluene into benzene. By controlling the flow of toluene to the hydrodealkylation plant, flexibility in the relative production rates of benzene and toluene may be achieved. Toluene disproportionation is an alternative process to hydrodealkylation; in this case the products are benzene and xylenes.

Part of the C₈-aromatics fraction from the main fractionation unit is superfractionated for the recovery of the required yield of o-xylene.

The boiling points of m-xylene, p-xylene and ethylbenzene are so close that they cannot economically be separated by fractionation. The important isomer p-xylene is separated from the C₈-aromatics mixture by crystallization or by selective adsorption on molecular sieves, leaving a m-xylene and ethylbenzene rich concentrate. This is fed to an isomerization plant, in essence a single reactor catalytic reforming unit, which converts ethylbenzene to xylenes and re-

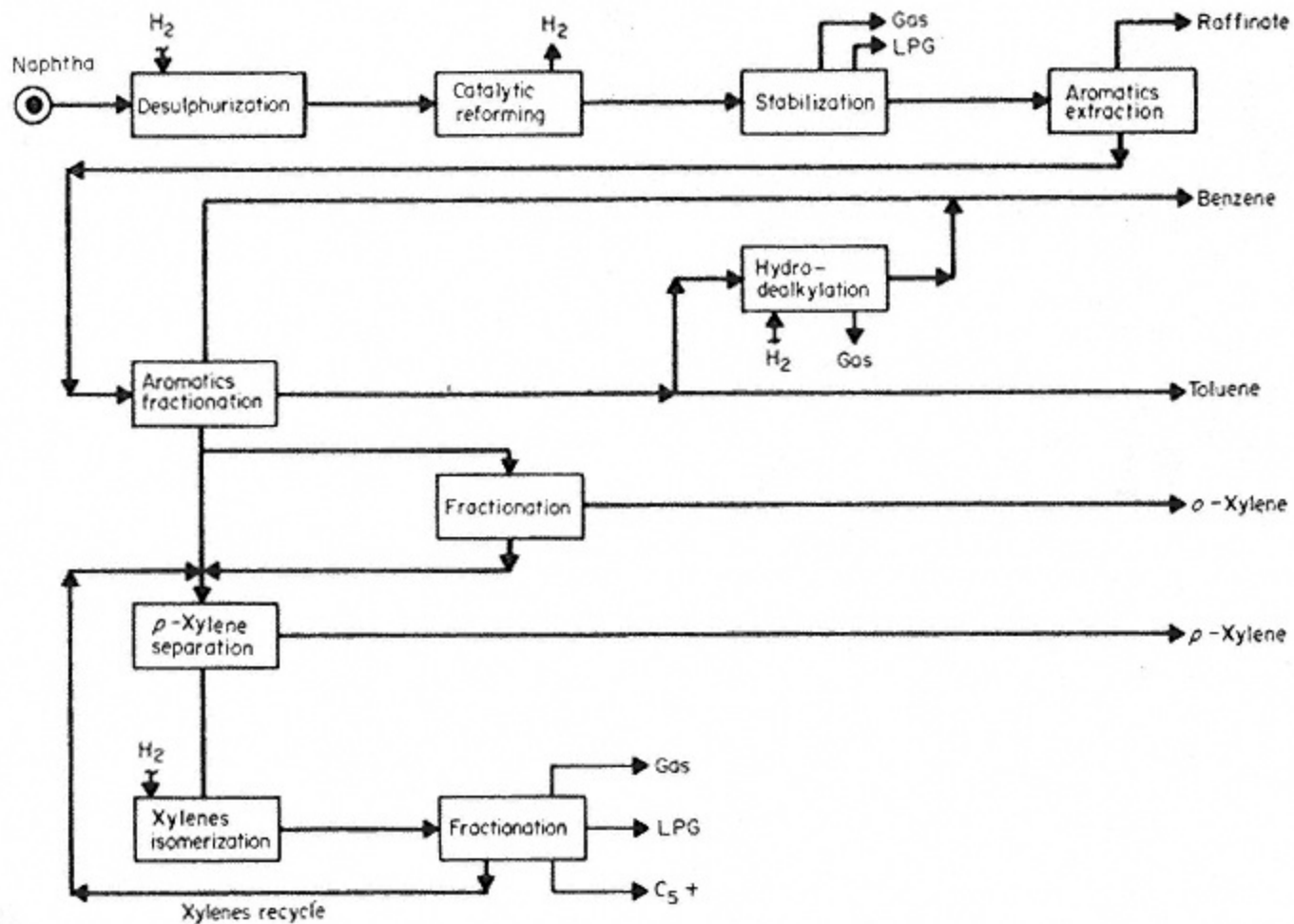


Fig. 5.
Typical block flow diagram for aromatics production.

TABLE 11 Typical Analysis of Pyrolysis Gasoline

	Wt.% on Pyrolysis Gasoline	Wt.% on Total Aromatics
Monoolefins	8	
Diolefins	15	
Saturates	7	
Benzene	32	46
Toluene	14	20
C8-aromatics	11	16
C9-aromatics	13	18
	100	100

establishes the xylenes equilibrium. By including the isomerization plant in a recycle loop, an increased yield of p-xylene may be taken at the expense of the m-xylene and ethylbenzene in the catalytic reformer. Mullarkey has shown that in those cases where p-xylene is the only isomer required, an overall yield of 87% may be recovered from a feedstock of the type shown in Table 10 [21]. Where o-xylene is also recovered, the overall yield of o-and p-xylenes may be well over 90%.

As pointed out in the section entitled "Olefins" above, aromatics may also be extracted from pyrolysis gasolines. The aromatics content of pyrolysis gasoline is a function of the composition of the feedstock and also the severity of pyrolysis. A representative breakdown based on the moderate severity pyrolysis of naphtha is shown in Table 11 [19].

When compared with the typical data quoted for catalytic reformat (Table 8 and Table 9), two significant differences become readily apparent.

In the first place, pyrolysis gasoline contains a far higher proportion of benzene for a similar total aromatics content than does catalytic reformat. The extra benzene is obtained at the expense of toluene and C8-aromatics.

The second, and very important point, is that the nonaromatics fraction of pyrolysis gasoline is highly olefinic. Indeed, it contains a high proportion of diolefins (cyclopentadiene in particular) which renders the raw gasoline unstable and liable to excessive gum formation in storage.

Cyclopentadiene may be separated from pyrolysis gasoline for the production of chlorinated insecticide (aldrin and dieldrin now no longer acceptable in Western Europe), for use in flame-resistant polyesters, or as the third comonomer in ethylene-propylene terpolymers (EPT rubbers).

In most cases, however, the as-produced pyrolysis gasoline is selectively hydrogenated to convert the diolefins to the corresponding monoolefins and thereby give a stable, high octane gasoline blendstock.

For aromatics extraction a second, more severe hydrogenation stage is also required to

fully saturate the olefins present and desulfurize the gasoline. Following this treatment, with suitable fractionation to take off nonaromatics

in the C5 and C9 and heavier boiling range, the "heart cut" is suitable for conventional aromatics extraction.

Synthesis Gas

The term "synthesis gas" refers to mixtures of hydrogen and carbon monoxide in any proportions. Synthesis gas is required for a number of petrochemical processes of which ammonia synthesis is by far the most important. Table 12 lists the main processes and the molar ratios of hydrogen/carbon monoxide (H_2/CO) required.

During the period when coal dominated the chemicals industry as the main raw material, synthesis gas was obtained by passing steam through red hot coke. Water gas, with a H_2/CO ratio of approximately 1.0, was thereby produced.

Two processes are now widely used for the manufacture of synthesis gas from petroleum fractions. These are steam reforming (of natural gas, light paraffinic hydrocarbons, or naphtha) and partial oxidation (of any petroleum stock but most usually of heavy residua).

Steam reforming gives a H_2/CO ratio in the range 2.0 (naphtha feed) to 3.0 (natural gas feed), while with partial oxidation of heavy residuum the H_2/CO ratio falls to less than 1.0.

The H_2/CO ratio of a synthesis gas can be increased by making use of the "shift" reaction in which carbon monoxide is reacted with steam to give hydrogen and carbon dioxide. The latter can be removed from the gas by washing it with a suitable solvent.

When the synthesis gas H_2/CO ratio is too high, as, for instance, when steam reformed methane is used for methanol synthesis, either carbon oxides are added from an outside source or the excess hydrogen must be purged from the synthesis reaction system.

In steam reforming a saturated, desulfurized, light hydrocarbon feedstock is mixed with steam, preheated, and passed over a nickel-based catalyst contained within externally heated tubes maintained at a temperature in the range of 750 to 900°C.

The gas leaving the reformer tubes consists of carbon monoxide and

TABLE 12 H_2/CO Required for Synthesis Gas User Processes

Process	H_2/CO Required
Hydrogenation (various), ammonia synthesis	No CO
Oxo synthesis	1.0
Methanol synthesis	2.0
Phosgene, organic acids, acrylates	No H_2

hydrogen (synthesis gas) together with some carbon dioxide, steam, and residual, nonreacted hydrocarbons. To minimize the hydrocarbon leakage, high temperatures and low operating pressures (10 to 25 bars) are desirable.

In the partial oxidation process, preheated feed is passed into a combustion chamber with a limited quantity of oxygen. The overall combustion reaction is exothermic and a temperature as high as 1400°C may be reached. Advantage is frequently taken of the fact that the process may be carried out at quite high pressures. Thus operation at 40 to 45 bars is common while designs for pressures as high as 175 bars have been proposed [22].

Some hydrocarbon pyrolysis occurs in the combustion chamber, and free carbon is always present in the reactor effluent. This is removed from the cooled gas by thoroughly washing it with water. The handling of the consequential soot/water slurry represents a significant problem to the plant designer.

Partial oxidation for synthesis gas production is generally economic only when petroleum feedstocks other than natural gas or naphtha must be utilized. Both steam reforming and partial oxidation are high temperature processes so efficient heat recovery systems form a vital part of the operating plant.

When producing ammonia, the synthesis gas generating facility is integrated with the gas purification and ammonia synthesis reactions of the plant.

Figure 6 shows a block flow diagram of a typical ammonia plant using the steam reforming process.

Feed desulfurization is an essential first stage as sulfur is a reformer catalyst poison. Most natural gases contain only traces of easily removed sulfur compounds, and zinc oxide is commonly used in this service. More refractory sulfur compounds, as found in naphthas, require more severe treatment such as hydrogenation over cobaltmolybdate catalyst followed by the reaction of the hydrogen sulfide so produced with zinc oxide.

The pretreated feed hydrocarbon is then mixed with steam and reformed in two stages. The primary reformer contains nickel catalyst in externally heated tubes as described earlier. Approximately 70% of the incoming hydrocarbon is converted in the primary reformer. The secondary reformer contains nickel catalyst in a fixed bed reactor. In this stage, process air is introduced into the system and partial oxidation of the primary reformer effluent increases the temperature of the gas and completes the reforming reaction. The quantity of air added to the secondary reformer is equivalent to the nitrogen requirement of the ammonia synthesis stage. The operating pressure of the primary/secondary reforming stages is typically 30 to 35 bars. The gas outlet temperature from the primary reformer is about 800°C and from the secondary reformer about 980°C .

From the secondary reformer the gas is passed to a shift converter system in which it is reacted with steam in two stages, first over promoted iron catalyst at 370 to 450°C and

then over copper/zinc catalyst at 210 to 240°C to reduce the carbon monoxide content to an acceptably low level and at the same time generate extra hydrogen.

This is followed by a carbon dioxide removal stage which may take many forms but is commonly a countercurrent scrubbing system with an amine or a hot, aqueous potassium carbonate solution as the absorption solvent. Carbon dioxide is liberated from the rich solvent by reboiling in a stripper column.

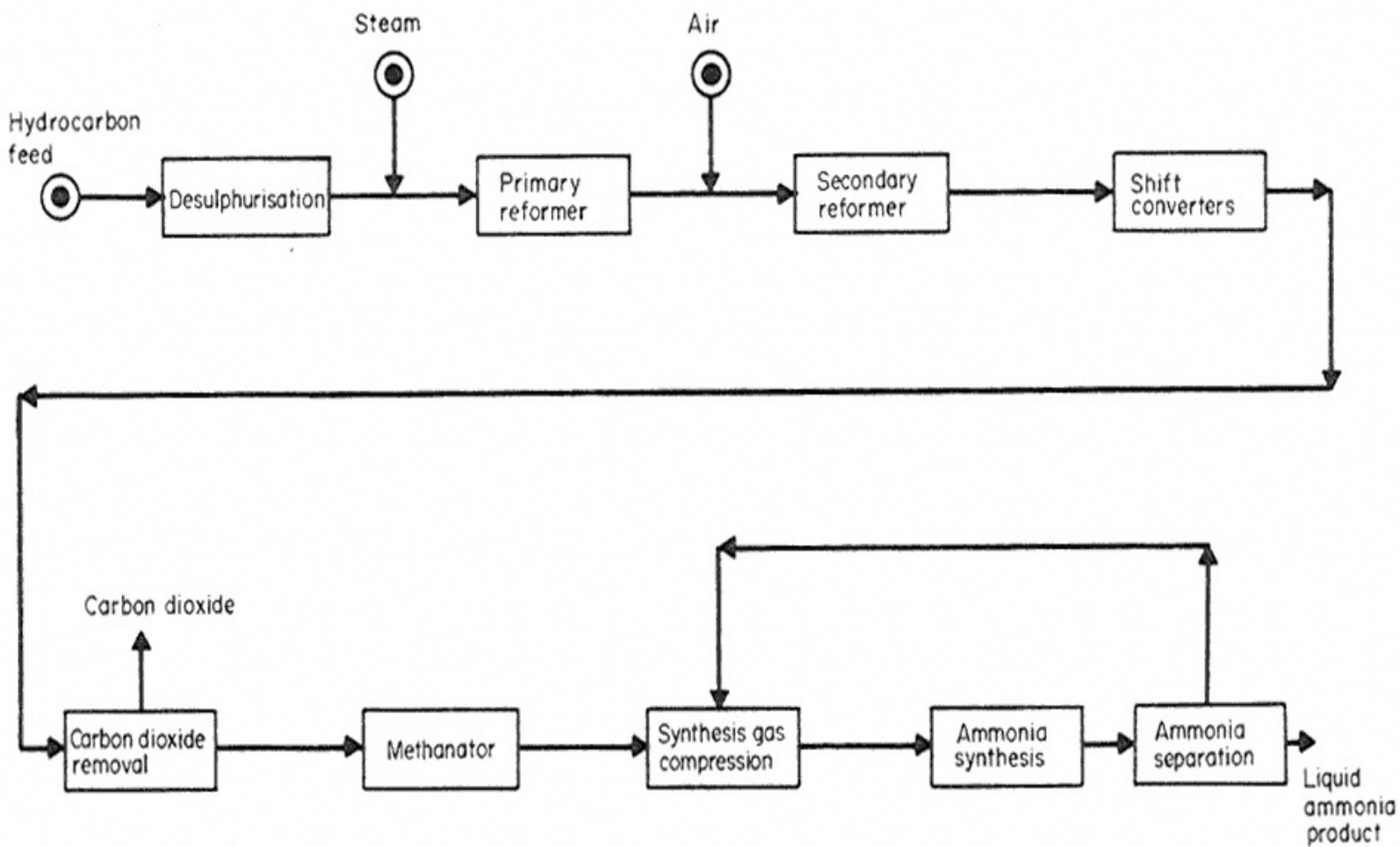


Fig. 6.
Typical block flow diagram for an ammonia plant.

TABLE 13 Primary IntermediatesMain Process Features

Process	Usual Features	Primary Products
Hydrocarbon pyrolysis	Ethane	Ethylene
	Propane	Propylene
	n-Butane	Butadiene
	Naphtha	Benzene
	Gas oil	Toluene
Catalytic reforming	Naphtha	Xylenes
		Benzene
		Toluene
Steam reforming	Natural gas	Xylenes
		Synthesis gas
Partial oxidation	Ethane	Synthesis gas
	Propane	
	Butane	
	Naphtha	
	Residuum	

At this point the nitrogen/hydrogen gas mixture contains only small quantities of carbon oxides, but as these are poisons to the ammonia synthesis catalyst they are reduced to extremely low levels (<5 ppm) by methanation.

The methanation stage is in effect a reverse steam reformer converting traces of carbon oxides to methane which is inert as far as the ammonia synthesis catalyst is concerned.

The purified nitrogen/hydrogen gas mixture, now containing just traces of methane and argon as impurities, is compressed to synthesis pressure (140 to 300 bars) and passed into the ammonia synthesis system. Partial conversion to ammonia takes place in the reactor over promoted iron catalyst. Ammonia is condensed from the effluent gases, and unconverted nitrogen and hydrogen are recycled. The inerts, methane and argon, tend to build up in the recycle gas and must be purged from the system.

Summary

The general features of the principal processes for the production of the three main categories of primary intermediates for the petrochemicals industry from petroleum-based raw materials are listed in Table 13.

Secondary and Higher Order Intermediates

With the exception of a few particular cases (such as polyethylene and polypropylene, which are made directly from their respective primary in-

intermediates), more stages of chemical processing are required to convert the primary intermediates into secondary and higher order intermediates, and it is from these that the final petrochemical end products are made.

The primary intermediates are relatively few in number, but the finished products can be counted in the thousands. Space permits no more than a general review of some of the more important process routes to the most widely manufactured products. These are presented in the Appendix and are considered under separate headings corresponding to the primary intermediate from which they are derived.

This listing is not complete by any means, but it does cover the main lines of the petrochemicals industry.

It shows that in each case a limited number of basic chemical processes such as chlorination, oxidation, and hydration are employed to produce a range of secondary intermediates which are, in general, more reactive than their respective primary intermediates. It is from the subsequent processing of the secondary intermediates that the complexity of petrochemicals processing arises.

This complexity is only too apparent. Process sequences involving four, five, or more separate and distinct stages are commonly needed, even for such wellknown, everyday products as nylon and synthetic detergents. In a complete petrochemicals installation producing a wide range of products, intermediate streams may be extracted from one process line and utilized in another; one plant's by-product may well be another's raw material. Each process unit involves not only a substantial capital investment on its own but also an extensive industrial infrastructure around it to provide supporting services, etc.

The planning of such facilities requires careful and detailed study to make the best use of all available resources to minimize material and energy losses and to ensure that safe, operable plants can, in fact, be constructed.

The listing in the Appendix also shows that there are alternative processing routes to some key intermediates. The selection of the best scheme for a particular application can pose problems not always apparent at first sight. An interesting example concerns the production of phenol, an important secondary intermediate in the production of phenol-formaldehyde, epoxy and polycarbonate resins, dyes, pharmaceuticals, agro-chemicals, etc.

Phenol is currently produced, commercially, by five proven processes (although a recent survey [23] lists, in fact, nine actual and potential process routes). These are entered in Table 14 which also indicates the starting raw materials and the main by-products where they exceed 10% of the phenol yield.

The most widely used processes for phenol today are based on the cumene route in

which there is a 60% yield of by-product acetone on phenol. The cumene route therefore relies on a substantial acetone market for the economic production of phenol; fortunately, this state of affairs has, in fact, existed for some time.

The chlorination route to phenol requires chlorine and caustic soda as principal reactants, producing by-product sodium chloride in yields on phenol of over 100%. The only way in which this process route can compete economically with others is when it is associated with an electrolysis plant to convert the sodium chloride back into chlorine and caustic soda. This implies a

TABLE 14 Main Commercial Routes to Phenol

Process Route	Raw Materials	By-products ^a
Cumene	Benzene Propylene	Acetone
Chlorination	Benzene Chlorine Caustic soda	Sodium chloride Dichlorobenzenes Substituted phenols
Hydrochlorination	Benzene	
Sulfonation	Benzene Sulfuric acid Caustic soda	Sodium sulfite
Oxidation	Toluene	

^aExcluding by-products yielding less than 10% on phenol.

cheap source of electric power. The chlorination process also produces significant yields of dichlorobenzenes and substituted phenols whose disposal must also be taken into account.

The hydrochlorination, or Raschig, process makes use of hydrogen chloride and air to produce monochlorobenzene which is hydrolyzed to phenol thereby regenerating hydrogen chloride, which is recycled. There are essentially no byproducts.

The sulfonation route is the oldest of all. It requires sulfuric acid and caustic soda as raw materials and produces large quantities of by-product sodium sulfite. If located close to a paper mill, the sodium sulfite can be utilized, otherwise it creates a serious disposal problem and processing debit.

The toluene oxidation route is the only commercial process not using benzene as a raw material. Because of its limited industrial applications and relative oversupply (by catalytic reforming), toluene is readily available in most aromatics production facilities. Indeed, a large proportion of all toluene presently produced is hydrodealkylated to convert it to the higher valued benzene. Toluene oxidation to benzoic acid, followed by the latter's oxidation to phenol with no by-products of significance, makes this route especially interesting in new petrochemicals complexes.

It may be concluded that when comparing processes for the production of phenol, for instance, much more than the immediate petrochemicals environment must be considered. The economic evaluation of alternative, competing process schemes must concern itself not only with internal supply and demand problems but also with possible interactions with other industries, and in some cases these can have a deciding influence on both process selection and site location.

This problem is common to much of the petrochemicals industry. Thus the supply of chlorine for vinyl chloride monomer production (for PVC) is associated with a caustic soda coproduct disposal problem which may or may not be acute depending on local demands for it. It also needs a relatively cheap

supply of electric power and be situated close to a source of salt brine. Caprolactam manufacture for nylon 6 production gives rise to by-product ammonium sulfate which explains the normally close association between caprolactam producers and the fertilizer industry.

A further feature of the petrochemicals industry affecting process selection is that many end products compete for the same market. This is clearly the case for products such as nylon 6-nylon 66 and high-density polyethylene-polypropylene.

In each case the physical properties of the end products are sufficiently similar, the production costs comparable, but the raw materials and/or the process routes are quite different. Thus it is not generally a simple matter to change to alternative products to match changes in market demand once a production line is established.

This gives a decided advantage to those companies who at the predesign stage make the best judgment as regards future trends in product requirements and take especial care over the planning of their new production facilities.

Interactions with Petroleum Refining

In discussing the complexity of petrochemicals processing in the last section, the importance of high-quality process planning at the predesign stage of the implementation of a petrochemicals installation was mentioned.

When the petrochemicals complex is associated with, or in some cases closely integrated into, a petroleum refinery, this need is even more severe. Clearly, the main purpose of a refinery is to produce petroleum products such as gasoline, kerosene, and gas oils for sale. A large olefins plant and catalytic reformer providing primary intermediates for a petrochemicals complex both require suitable hydrocarbon feedstocks and must compete for them in the normal refinery product market.

An olefins plant, in particular, can be designed to charge a wide range of hydrocarbon raw materials derived from many different sources within the refinery. The selection of the best stream or streams for pyrolysis in such a situation adds yet another burden to the process planner.

In an integrated petroleum refinery/petrochemicals complex recently studied in my own organization, in addition to the normal range of refinery products, a moderate range of petrochemicals and petroleum coke were included as required end products. In simple terms the problem was how best to produce the required products from a given crude oil within certain yield, quality, and financial constraints. More specifically, five basic interacting problems were required to be solved:

1. Which products should be produced?
2. How much of each product should be produced?

3. What process routes should be used (where alternatives exist)?

4. What raw materials should be used (where alternatives exist)?

5. How should the project be financed?

In tackling such a problem, certain minimum criteria need first to be specified. These include marketing strategies and sales forecasts, minimum and/or maximum yields of certain key products, availability and cost of capital at different total investment levels, economic objectives of the project, and any special constraints which may apply to the particular case under study.

Of these, the economic objectives must be especially clearly understood; typically they may be one of the following:

1. Minimization of investment for specific production goals
2. Minimization of production costs
3. Maximization of sales profit
4. Maximization of return on investment

Once these basic criteria have been established, the economics of the complex can be studied by constructing a mathematical model and subjecting it to computer optimization using the techniques of linear programming. The mathematical model defines, for each process under consideration, the relationships among capacity, investment cost, operating costs, and the constraints within which the process has to operate such as the availability of raw materials and product qualities.

Optimization by linear programming implies that the mathematical model must be composed of linear functions only. Ways of dealing with nonlinear functions, and in particular investment/capacity relationships, are now available and have been shown to give reliable results.

An integral part of such a study is postoptimization sensitivity analysis. Having obtained an optimized solution, the sensitivity of the solution to changes in the more important variables (such as product selling price and maximum product demand) are examined. The results of sensitivity analysis can be of importance in the final selection of process routes, raw materials allocation, etc.

The combination of advanced mathematical techniques and large, fast computers now enables the process planner to study, with confidence, many alternative processing schemes in a short space of time. Without such tools the planning of an integrated refinery/petrochemicals complex would be a haphazard affair and likely to result in a solution far removed from that obtained by proper economic optimization.

Summary

A brief review of the basic processing aspects of the petrochemicals industry has been

presented.

The emergence of the petrochemicals industry from petroleum refining in the 1920s has been shown, leading to the great expansion of the 1960s and 1970s.

It has been shown how the more important petrochemicals end products may be classified into seven main categories and the general properties of these have been described.

The way in which a relatively small number of primary intermediates gives rise to a progressively increasing number of secondary and higher order intermediates has been explained, and the principal process routes to the primary intermediates discussed.

An indication has been given of the complexity of petrochemicals processing and how this is magnified still further when interactions with petroleum refining are considered.

Ways in which process planners arrive at economically optimized process sequences for complete complexes have been outlined.

Appendix:

Main Derivatives of the Primary Intermediates

Main Ethylene Derivatives

Polymerization gives low-density and high-density polyethylene (LDPE and HDPE).

Copolymerization with propylene gives ethylene-propylene rubbers (EPR).

Copolymerization with propylene and a highly reactive third monomer such as cyclopentadiene gives ethylene-propylene terpolymer rubbers (EPT).

Chlorination and oxychlorination gives ethylene dichloride (EDC) which on dehydrochlorination gives vinyl chloride monomer (VCM) which on polymerization gives polyvinyl chloride (PVC).

Hydrochlorination gives ethyl chloride which reacts with sodium/lead amalgam to give tetraethyl lead (TEL) gasoline additive.

Hydration gives ethanol (synthetic alcohol) which apart from direct use as a solvent is oxidized to acetaldehyde which on oxidation gives peracetic and acetic acids used in the manufacture of cellulose acetate (rayon), vinyl acetate (adhesives, emulsion paints), acetate esters (solvents), and acetic salts (dyestuffs, fungicides). When condensed and dehydrated, acetaldehyde gives crotonaldehyde which on hydrogenation gives n-butanol (solvents, plasticizers, resins modifiers). When reacted with ammonia and formaldehyde, acetaldehyde gives pyridine and derivatives (dyes, pharmaceuticals, agrochemicals). Chlorination of acetaldehyde gives chloral, used as an intermediate for insecticides.

Oxidation gives acetaldehyde (see above) or under different reaction conditions ethylene oxide (EO) which on hydration gives ethylene glycol which, apart from use as antifreeze, is oxidized to glyoxal (permanent press fabric treatment) which reacts with dimethyl

terephthalate to give polyester fibers and film. By-product higher glycols are used as lubricants, solvents, and humectants. EO reacts with alcohols to give glycol ethers (solvents, thinners, brake

fluids, printing ink, plasticizers). EO reacts with ammonia to give ethanolamines (industrial solvents) and is also used as an intermediate for emulsifiers, detergents, corrosion inhibitors, waterproofing agents, and cosmetics.

Diethanolamine (DEA) on dehydration gives morpholine, used for corrosion inhibitors, emulsifiers, and solvents. EO reacts with higher alcohols and phenols to give nonionic detergents.

Alkylation of benzene with ethylene gives ethylbenzene which is dehydrogenated to give styrene which is polymerized to give polystyrene (plastics). Styrene is also copolymerized with butadiene to give styrene-butadiene rubbers (SBR), with acrylonitrile to give styrene-acrylonitrile (SAN) resins (high impact moldings), and with acrylonitrile and butadiene to give acrylonitrile-butadiene-styrene (ABS) resins (precision moldings, chromium-plated applications).

Main Propylene Derivatives

Polymerization gives polypropylene (PP) or, under different reaction conditions, the lower polymers, propylene trimer (nonenes), and propylene tetramer (dodecenes). Trimer reacts with carbon monoxide and hydrogen to give isodecanol which reacts with phenol to give diisodecyl phthalates (plasticizers). Trimer reacts with phenol to give nonyl phenol which reacts with EO to give nonionic detergents. Tetramer reacts with benzene to give dodecyl benzene which is sulfonated and neutralized to give nonbiodegradable detergents.

Copolymerization with ethylene gives ethylene-propylene rubbers (EPR). Copolymerization with ethylene and a highly reactive third monomer gives ethylene-propylene terpolymer rubbers (EPT). Codimerization with butylenes gives heptanes (solvents) which are carbonylated to give octanols.

Chlorination at high temperature gives allyl chloride. Allyl chloride reacts with hypochlorous acid to give dichlorohydrin which reacts with lime to give epichlorohydrin which when hydrolyzed with caustic soda gives glycerine (humectants, drugs, cosmetics, explosives). Glycerine reacts with phthalic anhydride to give alkyd resins and with diisocyanates to give polyurethanes. Epichlorohydrin reacts with diphenylol propane (bisphenol A) to give epoxy resins and phenoxy resins. Allyl chloride reacts with caustic soda to give allyl alcohol which reacts with hydrogen peroxide to give glycerine. Allyl alcohol copolymerizes with phthalic anhydride and cyanuric chloride to give special plastics.

Hydration gives isopropanol (solvents) which when dehydrated gives acetone (solvents) which condenses to form diacetone alcohol (DAA) (solvents) which on dehydration gives mesityl oxide which on hydrogenation gives methyl isobutyl ketone (MIBK) (solvents). DAA is hydrogenated to give hexylene glycol (brake fluids). Acetone reacts with phenol to give diphenylol propane (bisphenol A), used in epoxy resins and polycarbonate plastics.

Acetone reacts with hydrogen cyanide to give acetone cyanohydrin which is hydrolyzed with sulfuric acid to give methacrylamide sulfate which reacts with methanol to give methyl methacrylate monomer which is polymerized to polymethyl methac-

rylate (clear sheet plastics) and copolymerized with ethyl acrylate (acrylic paints) or with styrene-butadiene (high impact moldings).

Oxidation gives propylene oxide (PO) or under different reaction conditions, acrolein. PO is hydrated to give propylene glycol (cellophane plasticizer, humectants, hydraulic fluids) which reacts with dicarboxylic acids (phthalic, isophthalic, maleic) to give unsaturated polyester resins (glass reinforced moldings, boat hulls, etc.). PO reacts with polyfunctional alcohols to give polyethers or polyols which react with diisocyanates to give polyurethanes. PO reacts with propylene glycol to give polypropylene glycols (lubricants, cutting oils, inks, lacquers) which react with EO to give nonionic detergents. Acrolein reacts with isopropanol to give allyl alcohol which reacts with hydrogen peroxide to give glycerine.

Ammoxidation gives acrylonitrile which polymerizes to give acrylic fibers. Acrylonitrile copolymerizes with butadiene to give the nitrile rubbers, with styrene to give styrene-acrylonitrile (SAN) resins, and with butadiene and styrene to give acrylonitrile-butadiene-styrene (ABS) resins. Acetonitrile, produced as a by-product from the acrylonitrile process, is an industrial solvent and is used in the pharmaceutical industry (vitamin B₁, steroids).

Carbonylation or reaction with carbon monoxide and hydrogen (synthesis gas) gives n-butyraldehyde and isobutyraldehyde which on further hydrogenation give n-butanol (solvents, plasticizers, resin modifiers) and i-butanol (lube additives, solvents, plasticizers, resin modifiers). n-Butyraldehyde is oxidized to give n-butyric acid used in the manufacture of cellulose acetobutyrate (molding resins). n-Butyraldehyde is condensed, dehydrated, and hydrogenated to give 2-ethyl hexanol which reacts with phthalic anhydride to give 2-ethyl hexyl phthalate, a most important plasticizer for PVC.

Main Butadiene Derivatives

Polymerization gives polybutadiene rubbers (tire treads, natural rubber applications) and polybutadiene resins (tin plate lining, surface coatings).

Copolymerization with styrene gives styrene-butadiene rubber (SBR) (tires, shoes, foam rubber carpet underlay, adhesives, other rubber applications). Copolymerization with acrylonitrile gives nitrile rubber (oil-resistant applications) which when blended with PVC gives high impact molding resins. Copolymerization with acrylonitrile and styrene gives acrylonitrile-butadiene-styrene (ABS) resins (precision moldings, chromium-plated applications).

Chlorination gives a mixture of dichlorobutenes from which the 1,4-dichloro-2-butene isomer is separated. This reacts with sodium cyanide to give 1,4-dicyano-2-butene which when hydrogenated gives adiponitrile which on further hydrogenation gives hexamethylenediamine (HMD) which reacts with adipic acid to give nylon salt which polymerizes to nylon 66 (fibers, plastics). Under different chlorination conditions and with selective isomerization, 3,4-dichloro-1-butene may be separated. This is

dehydrochlorinated to give 2-chlorobutadiene or chloroprene which polymerizes to give polychloroprene or neoprene (cable insulation, adhesives, footwear, other rubber applications).

Main Butylenes Derivatives

Polymerization of isobutylene gives polyisobutylene (lube oil additives) or under different reaction conditions diisobutylene which reacts with phenol to give octyl phenol which condenses with EO to give nonionic detergents. Carbonylation of diisobutylene gives nonanols which react with phthalic anhydride to give plasticizers and with EO to give nonionic detergents.

Copolymerization of isobutylene and isoprene gives butyl rubber (tires, cable insulation, other rubber applications). Copolymerization of isobutylene and butenes give polybutylenes (lube oil additives, sealing compounds).

Hydration of butylenes gives sec-butanol (solvents) which is dehydrogenated to give methyl ethyl ketone (MEK) (solvents).

Dehydration of butenes gives butadiene.

Prins reaction with formaldehyde gives dimethyldioxane which is pyrolyzed to give isoprene which is polymerized to give polyisoprene (synthetic natural rubber).

Main Benzene Derivatives

Alkylation with ethylene gives ethylbenzene which is dehydrogenated to give styrene which is polymerized to give polystyrene (plastics). Styrene is also copolymerized with butadiene to give styrene-butadiene rubbers (SBR), with acrylonitrile to give styrene-acrylonitrile (SAN) resins, and with acrylonitrile and butadiene to give acrylonitrile-butadiene-styrene (ABS) resins. Alkylation with propylene gives isopropyl benzene or cumene which is oxidized to give cumene hydroperoxide and decomposed (cleaved) to give phenol and acetone. Phenol is copolymerized with formaldehyde to give phenol-formaldehyde (PF) resins. Phenol is chlorinated to give intermediates for dyes, insecticides, herbicides, antiperspirants, wood preservatives, and many other organic derivatives. Phenol reacts with acetone to give diphenylol propane (bisphenol A) used in epoxy resins and polycarbonate plastics. Phenol reacts with caustic soda to give sodium phenate which reacts with carbon dioxide to give sodium salicylate which on acidification gives salicylic acid, used to produce acetyl salicylic acid (aspirin), methyl salicylate (flavoring agent), and other salicylates (antioxidants, ultraviolet protection agents, pharmaceuticals). Alkylation with higher olefins such as propylene tetramer gives detergent alkylate which is sulfonated and neutralized to give nonbiodegradable detergents.

Hydrogenation gives cyclohexane which is oxidized to give a mixture of cyclohexanol and cyclohexanone. Oxidation of this mixture gives adipic acid which is reacted with ammonia to give adiponitrile which is hydrogenated to give hexamethylene diamine (HMD) which reacts with adipic acid to give a nylon salt which is polymerized to give nylon 66 (fibers, plastics). Further oxidation of cyclohexane gives cyclohexanone which reacts with

hydroxylamine sulfate to give cyclohexanone oxime which undergoes molecular rearrangement to give caprolactam which is polymerized to give nylon 6 (fibers, plastics). In addition to its nylon 66 use, adipic acid is used in the manufacture of plasticizers, synthetic lubes, and as a food additive.

Oxidation gives maleic anhydride which reacts with glycols to give polyester resins. Maleic anhydride reacts with hydrazine to give maleic hydrazide (herbicides) and is used as an intermediate in the production of malathion (insecticides). Maleic anhydride reacts with butadiene to give tetrahydrophthalic anhydride (THPA) which reacts with polyhydric alcohols to give alkyd resins and is also used as an intermediate in the production of captan (fungicide). Maleic anhydride is hydrogenated to succinic anhydride which is used in the manufacture of pigments and lube additives.

Nitration gives nitrobenzene which on reduction gives benzidine, an important intermediate in the manufacture of synthetic dyes. Nitrobenzene can also be hydrogenated to give aniline, another important intermediate for dyestuffs, drugs, antioxidants, rubber additives and polyurethane foams, etc.

Chlorination gives benzene hexachloride (BHC) (fungicides and insecticides). Under different reaction conditions monochlorobenzene is produced which reacts with caustic soda to give sodium phenate which on acidifying releases phenol. Oxichlorination with hydrogen chloride and oxygen also produces monochlorobenzene which when hydrolyzed gives phenol and recycle hydrogen chloride.

Sulfonation gives benzene sulfonic acid which is neutralized with sodium sulfate and the sodium benzene sulfonate fused with caustic soda to give sodium phenete which when treated with sulfur dioxide gives phenol.

Main Toluene Derivatives

Nitration gives dinitrotoluene which is hydrogenated to toluene diamine which reacts with phosgene to give tolylene diisocyanate (TDI) which reacts with polyols to give polyurethane foams. Nitration under different reaction conditions gives trinitrotoluene (TNT) explosive. Under still different reaction conditions nitration gives mononitrotoluenes which are widely used as intermediates for dyestuffs, pharmaceuticals, optical bleaches, etc.

Oxidation gives benzoic acid used in the dyestuffs industry and, as the sodium salt, as a foodstuffs preservative. Benzoic acid is hydrogenated to give hexahydrobenzoic acid which reacts with nitrosyl sulfuric acid to give caprolactam which is polymerized to give nylon 6 (fibers, plastics). Benzoic acid is neutralized with caustic potash to give potassium benzoate which undergoes disproportionation to give benzene and potassium terephthalate. The latter is made to produce terephthalic acid (TPA) for polyester production. Benzoic acid oxidation provides an alternative route to phenol.

Chlorination products are intermediates for the production of perfumes, dyestuffs, herbicides, and pesticides. Under different reaction conditions benzyl chloride is formed which is used to make butylbenzene phthalate (PVC plasticiser). Benzyl chloride is hydrolyzed to benzyl alcohol (perfume) which is reacted with sodium cyanide to give benzyl cyanide which is hydrolyzed to give phenylacetic acid. This is used for

pharmaceuticals (penicillins, amphetamine). Benzyl cyanide is used in the manufacture of phenobarbitone hypnotic.

Chlorosulfonation gives o- and p-toluene sulfonyl chlorides (plasticizers). The ortho isomer is used to make saccharin.

Main Xylenes Derivatives

Oxidation of o-xylene gives phthalic anhydride, the esters of which are the most used plasticizers. When reacted with polyhydric alcohols, phthalic anhydride gives alkyd resins. Phthalic acid derivatives are used for dyestuffs (anthraquinones, phthalocyanines). Oxidation of p-xylene gives terephthalic acid which reacts with methanol to give dimethyl terephthalate which reacts with ethylene glycol to give polyester fibers and film.

Main Synthesis Gas Derivatives

Carbonylation of olefins (oxo reaction) leads to aldehydes of one higher carbon number than the olefin, thus propylene gives butyraldehydes, heptenes give octylaldehydes, etc. The process is utilized to give higher aldehydes and hence higher alcohols for plasticizers, nonionic detergents, etc.

Synthesis of ammonia leads to nitrogenous fertilizers and nonfertilizer uses of ammonia in fibers, plastics, resins, chemicals, and explosives. Ammonia reacts with carbon dioxide to give urea (fertilizers) and which copolymerizes with formaldehyde to give urea-formaldehyde (UF) resins. Urea is selectively decomposed to give cyanic acid which is condensed to give melamine resins (laminates, moldings). Ammonia is oxidized to give nitric acid used widely in the chemicals industry. Under different reaction conditions oxidation of ammonia gives hydrazine (rocket fuel) which reacts with urea to give semicarbazide (pharmaceuticals) and which is oxidized to give azodicarbonamide a blowing agent for plastic foams. Methanol is synthesized from carbon oxides and hydrogen in synthesis gas and is oxidized to formaldehyde which is copolymerized with phenol and urea to give phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins. Formaldehyde reacts with ammonia to give hexamethylene tetramine (HMTA), used as a source of formaldehyde in PF molding powders and in the pharmaceuticals industry. Formaldehyde reacts with acetaldehyde to give pentaerythritol which reacts with polyhydric alcohols to give alkyd resins and is used in the manufacture of explosives, synthetic lubes, and floor polishes. Methanol reacts with ammonia to give methylamines. Monomethylamine (MMA) is used to produce insecticides and pesticides. Dimethylamine (DMA) is used in the production of solvents for fiber spinning and chemicals for the rubber industry. Trimethylamine (TMA) is used in the production of choline salts for poultry feed. Methanol reacts with hydrochloric acid to give methyl chloride which is used to make silicones and tetramethyl lead (TML) gasoline additive.

Chlorination of carbon monoxide gives phosgene which reacts with primary amines to give isocyanates which are used for pesticides, pharmaceuticals, and textile chemicals manufacture. Phosgene reacts with toluene diamine to give tolylene diisocyanate which reacts with polyols to give polyurethane foams. Phosgene reacts with the sodium salt of bisphenol A to give polycarbonate resins.

Hydrogen derived from synthesis gas is used for many hydrogenation reactions and in the production of hydrogen peroxide (bleaches, other chemicals, rocket fuels, epoxide resins).

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Gas Processing

Edited by John J. McKetta

Gas processing volumes and products production in the United States still show residual effects from the prolonged recession. Worldwide totals were similarly affected as values also declined for both gas throughput and products production.

For the first time, total products production in the United States was less than that of the combined total for the rest of the world. However, the United States is still out in front in the number of plants, capacity, and actual throughput. Gas processing has truly become an international industry.

Reflected in the United states production of natural gas liquids (NGL) was the greater use by olefin producers of lighter feedstock in 1983. In contrast to all other products, ethane output was higher by a small amount (Fig. 1).

Reported ethane production in 1983 averaged 76,200 gal/d higher than the year before, an increase of 1.37%. All other categories were lower, and the total of all products production decreased an average of almost 6 million gal/d, a drop of slightly under 10% (Table 1).

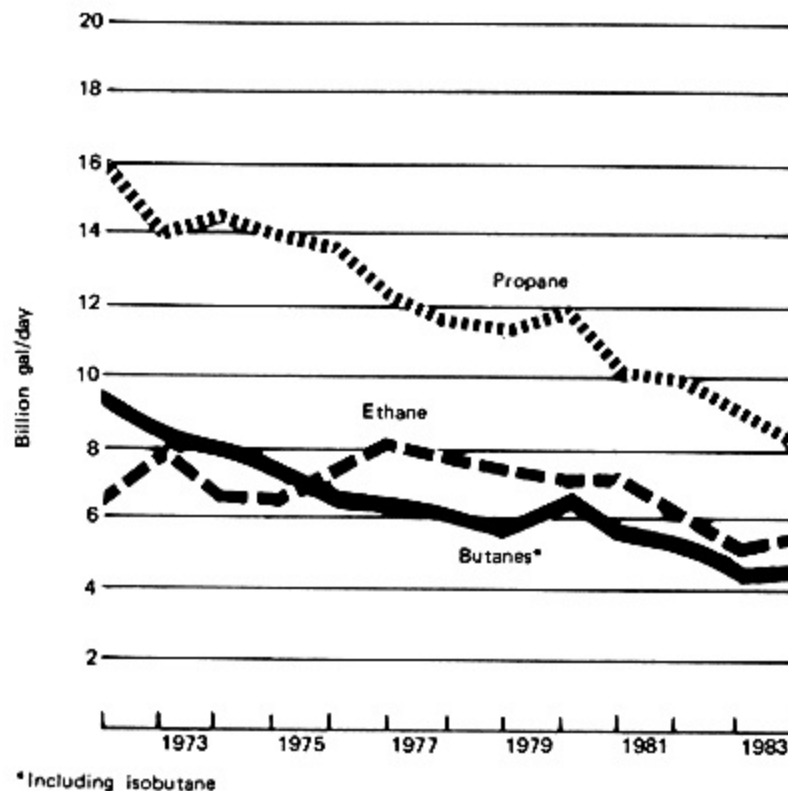


Fig. 1.
United States key products production.

TABLE 1 United States Gas Liquids Production

	1000 gal/d			
	1982	1983	Change	% Change
Ethane	5,551.1	5,627.3	+76.2	+1.37
Propane	8,789.1	8,106.1	-683.0	-7.77
Isobutane	1,170.8	1,164.1	-6.7	-0.57
Butanes	3,604.7	3,514.9	-89.8	-2.49
LP-gas mix	3,938.2	1,582.9	-2,355.3	-59.81
Raw NGL mix	29,350.9	27,646.0	-1,704.9	-5.81
Debut natural gasoline	4,658.0	3,840.7	-817.3	-17.55
Other	4,056.9	3,689.3	-367.6	-9.06
Total	61,120.1	55,171.3	-5,948.8	-9.73

The number of plants that were on-stream continued to increase in the United States to 880 from 859 (Fig. 2), and to 487 from 466 in the rest of the world, which included a jump in Canada to 346 from 337 (Fig. 3). But while the number of plants in the United States went up last year, they represented less capacity for the second year in a row, down to 68.9 billion CFD from 70.5 billion CFD.

Throughput also dropped, to 37.6 billion CFD from 41.2 billion CFD in the United States (Fig. 4), and to 11.6 billion CFD from 12.2 billion CFD in Canada (Fig. 5). Even an increase to 25.8 billion CFD from 23.9 billion CFD in the rest of the world was not enough to keep total throughput from going down.

Gas liquids production in Canada, like the United States, was lower in 1983, dropping an average of 6.56%, compared to 1982, down to 14.2 million gal/d from 15.2 million gal/d. In the rest of the world (excluding the Communist areas), products production was up by 2.3 million gal/d, an increase of 5.2% (Table 2, Fig. 6).

LPG Trade Anticipated

Much of the NGL produced in areas outside the United States and Canada is for export, particularly the LPG (mainly propane and butane). Some 18 million tons of LPG moved in long-haul trade in 1983 [1]. Approximately 10 million tons came from the Arab Gulf, 2 million from the North Sea, 1.3 million from Australia, and 1 million tons from Yanbu on the west coast of Saudi Arabia. About 75% of the Arab Gulf exports went to Japan and 3% to the United States. Northwestern Europe imported about 10% of the Arab Gulf's exports.

United States imports of LPG could increase substantially by the end of the decade, by nearly 3.2 million tons between 1983 and 1990. By one estimate, consumption as ethylene feedstock could increase by 4.0 million tons, assuming that LPG is priced to compete with naphtha.

One of the key challenges to gas processors will be to keep prices competitive. Since many of the newer heavy-liquids crackers in the United States have been revamped to

crack considerable quantities of ethane and propane,

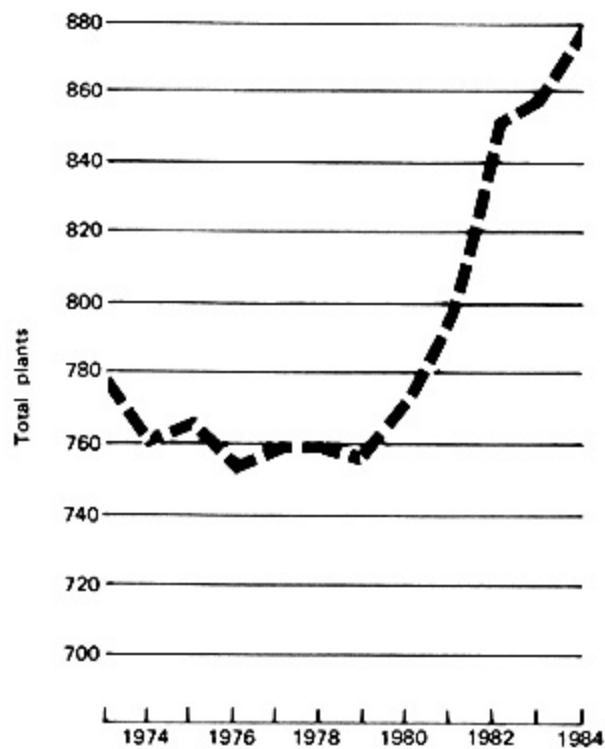


Fig. 2.
United States gas-processing plants
(as of January 1, 1984).

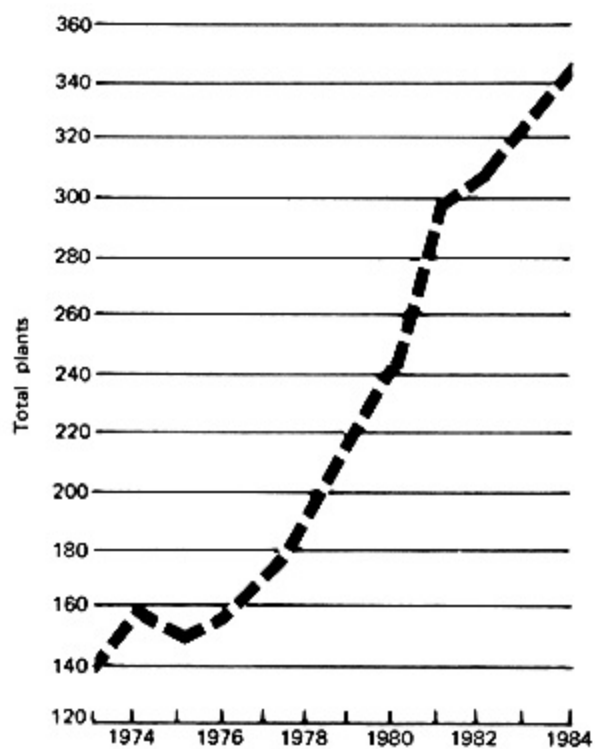


Fig. 3.
Canadian gas-processing plants
(as of January 1, 1984).

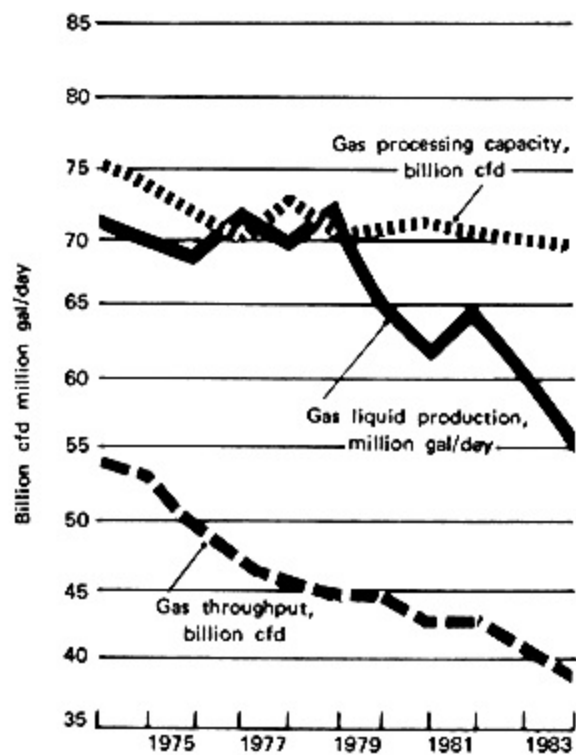


Fig. 4.
United States gas-processing trends.

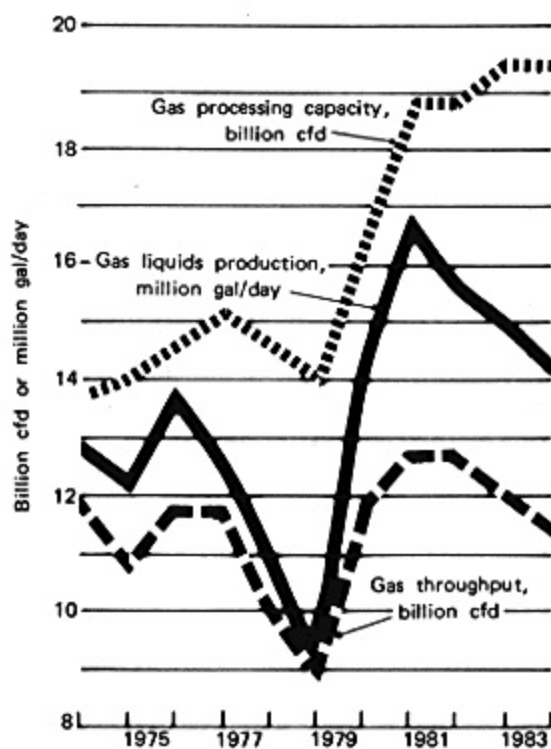


Fig. 5.
Canadian gas-processing trends.

TABLE 2 Processing and Reserves

	1982	1983	Change	% Change
United States:				
Gas throughput, MMCFD	41,156.9	37,576.8	-3,580.1	-8.70
Gas liquids production, 1000 gal/d	61,120.1	55,171.3	-5,948.8	-9.74
Proven gas reserves, billion ft ³	204,000.0a	198,000.0b	-6,000.0	-2.94
Canada:				
Gas throughput, MMCFD	12,227.8	11,580.4	-647.4	-5.29
Gas liquids production, 1000 gal/d	15,207.3	14,209.1	-998.2	-6.56
Proven gas reserves, billion ft ³	97,000.0a	90,500.0b	6,500.0	-6.70
Rest of the world:c				
Gas throughput, MMCFD	23,901.8	25,768.4	+1,866.4	+7.8
Gas liquids production, 1000 gal/d	44,121.8	46,421.1	+2,299.3	+5.21
Proven gas reserves, billion ft ³	1,448,727.0a	1,464,650.0b	+15,923.0	+1.10

aAs of January 1, 1983.

bAs of January 1, 1984.

cExcluding Communist areas.

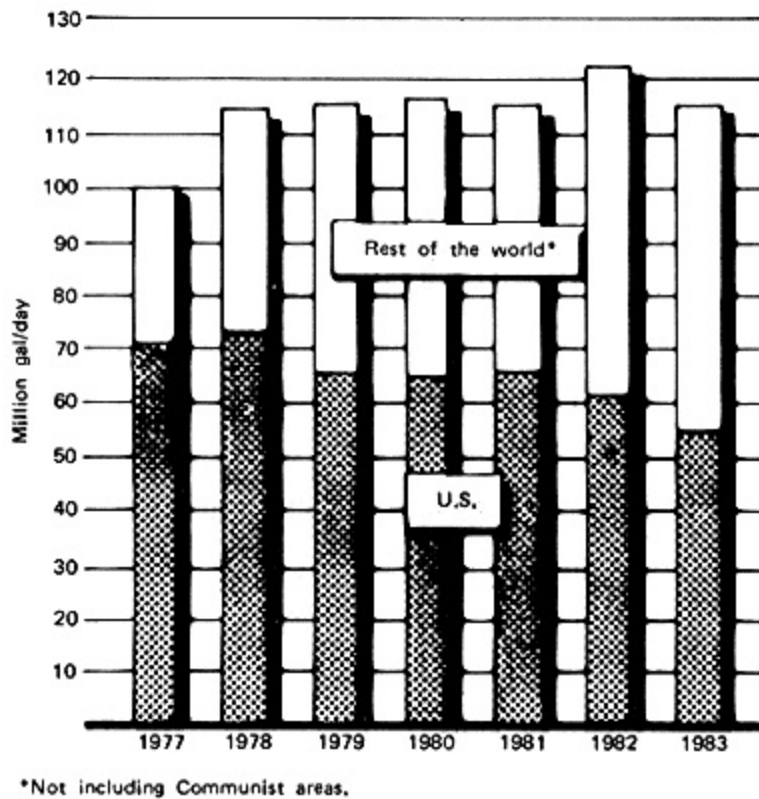


Fig. 6.
Gas products production.

tremendous flexibility exists within the industry to take advantage of changing feedstock economics. Similar changes have been made at installations in Europe, with an eye on increased NGL from North Sea production.

United States ethane requirements for ethylene production could actually swing between 245,000 to 584,000 bbl/d, compared to today's average rate of approximately 380,000 bbl/d.

Worldwide LPG is expected to be essentially in relative balance over the rest of the decade, according to one economic study group [2]. In contrast to earlier projections of large world surpluses, reduced projections of world oil demand and crude oil production have changed the outlook. Even so, LPG could expand its markets by as much as 25% by 1990.

Areas outside the United States are expected to be the main growth locations, representing nearly 80% of a projected growth in LPG demand of about 2.42.7%/yr. These areas will include Japan, the Far East, Europe, and Latin America.

Actual volumes of future LPG supplies will depend on the timing and capacity of new gas-processing plant construction. Worldwide, there were five more plants listed in 1983 than in the year earlier survey (Table 3). Totals for the respective years were 77 and 72 plants under construction or planned,

TABLE 3 Worldwide Gas Processing-Plant Construction^a

Area	1983	1984	Change
United States	21	20	-1
Canada	8	11	+3
Latin America	10	10	
Europe	12	10	-2
Middle East	4	10	+6
Africa	4	4	
Asia-Pacific	13	12	-1
Total	72	77	+5

^aUnder construction or planned, including expansions.

including expansions. Canada and the Middle East accounted for the increase, balancing fewer projects in all other areas.

The Tabasco plant in Mexico is on-stream, with a total capacity at this location of 2.5 million tons/year.

In Algeria, the first train of Jumbo 1 is on-stream. The installation has four identical trains, with a total capacity of 4.0 million tons. A second, similar plant, is scheduled but might not be constructed.

Malaysia became an LPG exporter in 1985 and exports from the Braefoot Bay plant started then as well. This plant has a 1.2 million ton/year capacity. Australia's Port Bonython LPG plant started up in 1985.

Associated gas from the medium and heavy crude oil fields in Saudi Arabia are being connected to the master gas system, starting this year. Hookups are scheduled to run through 1986.

In general, less gas is associated with medium and heavy crudes than with light crudes. Some liquids will also be recovered from nonassociated gas that is being developed for domestic use to assure that there will be ample gas for scheduled petrochemical projects.

Production Leaders

Of the United States gas and NGL producers, Texas ranks number one for all categories: gas throughput, capacity, number of plants, and production (Table 4). Texas' throughput of just over 12,500 MMCFD was 33.32% of the United States total. NGL production, nearly 24.8 million gal/d, was about 45% of total products. Louisiana, the 1982 leader in gas throughput, was in the number two spot in 1983, with 30.84% of throughput, and 17.86% of products production. Ranking third is Oklahoma with 10% of NGL production, but only slightly over 7.6% of throughput.

Texas and Louisiana together account for more gas throughput and liquids production than the rest of the top eight producing states combined. In NGL production, Oklahoma is followed by New Mexico (6.97%), Kansas (3.52%), Wyoming (3.05%), California (2.32%), and Florida (0.68%). All told,

TABLE 4 Major United States Gas-Producing States in 1983

	Gas Throughput (MMCFD)	% of Total Throughput	Gas Capacity (MMCFD)	% of Total Capacity	No. of Plants	% of Total NGL Production	
						Plants	1000 gal/d
Texas	12,519.20	33.32	23,504.6	34.09	415	47.16	24,782.40
Louisiana	11,587.00	30.84	22,194.5	32.19	106	12.05	9,852.30
Oklahoma	2,866.3	7.63	4,857.60	7.05	104	11.82	5,570.3
Kansas	2,704.9	7.20	4,901.50	7.11	25	2.84	1,942.4
New Mexico	2,051.2	5.46	3,683.30	5.34	44	5.0	3,845.4
Wyoming	1,105.4	2.94	1,912.0	2.77	40	4.55	1,683.10
Florida	766	2.04	961.50	1.39	3	0.34	374.00
California	715.50	1.90	1,483.10	2.15	37	4.20	1,280.10
Subtotal	34,315.5	91.32	63,498.7	92.10	774	87.95	49,330.00
Other states	3,261.3	8.68	5,444.3	7.90	106	12.05	5,841.3
Total	37,576.8		68,943.0		880		55,171.3

these eight states turn out nearly 90% of the United States NGL product and account for over 90% of gas capacity and throughput.

In Canada, Alberta has nearly all the gas-processing plants, 327 out of a total of 346. It therefore supplies virtually all of the just over 14 million gal/d of gas liquids production and accounts for 10.7 billion CFD of the country's 11.6 billion CFD of gas throughput.

Outside the United States and Canada, the leading countries in gas throughput in this year's list are Algeria (4.3 billion CFD), Mexico (3.5 billion CFD), and Italy (3.2 billion CFD). Italy has slightly more gas processing capacity than Algeria. Early predictions for 1984 (Oil and Gas Journal, p. 95, January 30, 1984) placed demand for LPG and ethane in the United States increasing 3%. Recovery will be due mainly to resurgence in the petrochemical sector. Even so, the liquids recovery rate/MCF of gas processed will drop.

If demand recovers in other areas as well, gas liquids output could make a comeback, particularly as new petrochemical facilities come on-stream in the hydrocarbon-rich areas of the world where flared gas will be recovered in larger and larger quantities to feed them.

And it is in some of these areas that the largest reserves of natural gas liquids are to be found. The Institute of Gas Technology estimates [3] worldwide NGL proved and currently recoverable reserves, as of December 31, 1982, at 79.1 to 97.1 billion bbl.

NGL reserves in Asia, including the Middle East, are far and away the largest, estimated at 24.0132.94 billion bbl. The USSR is credited with 3036 billion bbl, while North America has 8.53 billion bbl and Latin America 5.335.81 billion bbl, according to the IGT estimate. Africa has about the same, 5.726.77 billion bbl.

Processing Challenges

Enhanced oil recovery (EOR) could account for as much as 1 million bbl/d of United States crude oil production by 1990 (Oil and Gas Journal, p. 59, April 23, 1984). Big contributors will be miscible CO₂ flood and nitrogen injection projects. As injected CO₂ or N₂ reappear in the associated gas, they represent new processing challenges for the gas processor. Already, new products and technology are being developed to meet this challenge. Among these are membrane applications, both alone and in combination with new and existing, more-conventional approaches.

In terms of conventional processing choice, the clear leader for a number of years for new plants has been the turboexpander. Since 1980, the number of turboexpander installations in the United States has increased almost 55%, going from 207 to 322 (Table 5). This approach wasn't the percentage leader in increases, however. The number of compression-based processes doubled, from 8 to 16. Installations of Joule-Thomson cryogenic processes went up 13, a 57% gain, and refrigeration units jumped by 25, a 14.5% increase of the 173 that were listed before.

The largest decrease in number was in refrigerated absorption processes. There are now 54 fewer installations than there were in 1980, dropping to 240 from 294, over 18%.

TABLE 5 United States Extraction Processes

	Number of Installations ^a		Change	% Change
	1980	1983		
Expander	207	322	+115	+55.56
Refrigerated absorption	294	240	-54	-18.37
Refrigeration	173	198	+25	+14.45
Absorption	82	58	-24	-29.27
Joule-Thomson	23	36	+13	+56.52
Adsorption	37	22	-15	-40.54
Compression	8	16	+8	+100
Total installations	824	892	+68	+8.25

^aTotal process installations are greater than the number of total plants since more than one process is used at some locations.

Hindered amines are a newly introduced product class that can provide more efficient, selective separations of H₂S and CO₂ from the associated gas stream and from each other. Another approach is through different solvent/amine combinations or selective distillations.

Membrane-based processes come into their own at higher CO₂ levels, acting to pull out most of the CO₂ so that the gas can be processed in existing equipment. Another gas processing challenge is being met in the recovery of CO₂ from other than natural sources. Economical separations from flue gas and compressor exhaust are now being practiced.

A pending future technical challenge to the gas processor is now being considered by the U.S. Environmental Protection Agency. The EPA is proposing standards to tighten hydrocarbon and sulfur dioxide emissions from natural gas processing and treatment plants.

The standards would reduce leaks of volatile organic compounds from equipment by about 78%. The standards would cover leaks from each new, modified, and reconstructed compressor or gas processing unit onshore. Also included would be pumps, valves, pressure relief devices, open-ended valves and lines, and flanges and connectors.

Sulfur dioxide rules would cover each new or modified sweetening unit at onshore natural gas handling facilities. Because plant characteristics vary considerably, EPA is setting multiple emission limits. Applicable limits would be determined by the H₂S/CO₂ ratio and sulfur feed rate. Sweetening units producing less than 1 long ton/day of sulfur would not be subject to the control requirements.

Less Natural Gas

For the third year in a row, worldwide production of natural gas was less than the year before (Table 6). Communist areas, with the USSR leading the way, logged an increase. So did Western Europe and Latin America.

TABLE 6 World Gas-Production Trends (billion ft3)

	1976	1977	1978	1979	1980	1981	1982	1983	% Change 1983 vs 1976
United States	19,992.8	20,337.5	19,922.4	19,999.4	20,267.0	19,596.0	18,731.0	16,581.0	-11.5
Western Europe	6,239.1	6,290.7	4,793.7	6,866.6	6,668.7	6,906.6	6,142.1	6,363.4	+3.9
Canada	3,157.2	3,301.4	3,133.1	3,646.5	2,668.3	2,546.1	2,414.1	-5.2	
Latin America	2,044.4	2,116.3	2,533.5	2,610.0	3,297.5	3,071.5	3,340.5	+8.8	
Middle East	2,003.1	2,789.7	2,604.4	1,624.7	1,221.3	1,542.0	1,799.7	1,633.0	-9.3
Asia-Pacific	982.0	1,267.6	1,640.1	1,827.9	1,558.4	2,765.0	2,176.6	2,187.7	+0.5
Africa	1,628.3	1,780.7	1,558.1	1,027.9	884.1	1,947.0	1,168.9	1,143.8	-2.2
Communist area	14,360.6	15,999.8	17,683.3	19,591.4	21,069.9	19,210.0	20,258.0	21,383.0	+5.6
World total	50,407.5	53,883.7	53,859.5	57,194.6	58,636.4	57,816.0	55,893.9	55,665.0	-1.5

TABLE 7 World's 20 Top Gas-Producing Countries in 1983

Country	Production (109 ft ³)	Share (%)
USSR	18,903.0	34.33
United States	16,581.0	30.11
Netherlands	2,678.9	4.87
Canada	2,414.1	4.38
Mexico	1,479.5	2.69
United Kingdom	1,395.3	2.53
Romania	1,200.0	2.18
Norway	861.4	1.56
Algeria	707.0	1.26
West Germany	605.2	1.10
Venezuela	559.2	1.02
Argentina	549.6	1.00
Iran	500.2	0.91
Indonesia	481.8	0.88
Italy	450.1	0.82
Australia	423.5	0.77
Saudi Arabia	381.5	0.69
China	371.0	0.67
Pakistan	341.4	0.62
Brunei	316.3	0.57
Top 20	51,200.0	92.98
Others	3,866.5	7.02
Total	55,066.5	

Production in the USSR was up to 18.9 trillion ft³ from 17.69 trillion ft³, making it the leading country in natural gas production.

These gains were more than offset by a sharp drop in the United States where natural gas output was down 11.5% in 1983, compared to a year earlier. Production dropped to 16.58 trillion ft³ from 18.73 trillion ft³.

Canada, the Middle East, and Africa also turned out lower volumes than a year earlier. Canada's drop was for the fourth year in a row, going down to 2.41 trillion CO₂ from 2.55 trillion ft³.

Of the world total of 55.066 trillion ft³, the USSR and the United States account for nearly 65%. Soviet Union was the world leader in gas production for the first time in 1983, with 34, 33% of the total, compared to 31, 64% of 1982 production. The United States dropped to second place, now accounting for just over 30% (Table 7).

The Netherlands, Canada, Mexico, the UK, and Romania come next in order among the 20 most productive countries, ranging in share from The Netherlands' 4.87% to Romania's 2.18%. No other country has as much as 2% of the world total. However, these 20 countries produce nearly 93% of the world total.

As with gas liquids reserves, the USSR is the leading country in natural gas reserves, 1400 trillion ft³ (Table 8). This is almost 44% of the world's proven reserves. Iran is second with 15%, followed by the United States at about 6.2%. Saudi Arabia's listed reserves of 121 trillion ft³ put it in fourth place (3.78%), just ahead of Algeria (3.44%). Canada (2.83%), Mexico (2.36%), Qatar

TABLE 8 World's Major Gas Reserves (as of January 1, 1984)

	Estimated proved reserves (1012 ft ³)	Share (%)
USSR	14,000.0	43.75
Iran	480.0	15.00
United States	198.0	6.19
Saudi Arabia	121.0	3.78
Algeria	110.2	3.44
Canada	90.5	2.83
Mexico	75.4	2.36
Qatar	62.0	1.94
Norway	58.8	1.84
Venezuela	54.55	1.71
Netherlands	50.05	1.56
Malaysia	48.0	1.50
Nigeria	34.8	1.09
Kuwait	31.0	0.97
China	30.3	0.95
Indonesia	30.2	0.94
Iraq	29.0	0.91
United Kingdom	25.1	0.78
Argentina	24.4	0.76
Libya	21.35	0.67
Abu Dhabi	20.5	0.64
Australia	17.7	0.55
Subtotal	3,012.85	94.15
Others	187.1	5.85
Total	3,199.95	100.0

(1.94%), Norway (1.84%), and Venezuela (1.71%) round out the top 10. Again, the top 20 countries have nearly 94% of the world total.

According to the American Gas Association, 1983 gas reserve addition replacement levels topped 106% of production. Preliminary findings show that domestic gas reserves about equaled or exceeded production for the third year in a row.

AGA president, George H. Lawrence, said that average reserve additions over the past three years have been 107% of production. He looks for the current supply deliverability surplus to last for the next two years. After that, supply and demand will come to balance, and remain so.

A somewhat different scenario was projected by Merrill Lynch, Pierce, Fenner & Smith who believe the United States could experience a shortage of gas supply from domestic sources in 1985-1986. A good, positive reaction to such a development would be a sharp increase in gas well drilling in 1986.

The firm bases its forecast on a projected dramatic increase in consumption coupled with

a deliverability capacity that is generally overstated, possibly by as much as 35%. "The surplus is fragile at best," the company said.

Future Trends

Since 1973, data on United States energy production and use show:

Marketed natural gas production has declined 26%.

Total petroleum consumption has declined 14%.

Total United States energy consumption has declined 5%.

Total energy consumption/dollar of gross national product (in 1972 dollars) has declined 22%.

Total oil and gas consumption/dollar of gross national product has declined 32%.

Natural gas consumption for power generation has declined 21%; oil consumption for power generation is down 57%.

Petroleum products used for transportation have actually increased about 3 1/2%; however, 1983 transportation use was down approximately 10% from its 1978 peak.

There are numerous explanations for these changes. Among them are two severe price shocks during the 1970s, increasingly rigid environmental regulations, two very severe economic recessions, and various other events.

Gas Processing Changes

Having reviewed some of the major trends in the overall petroleum industry, it may be instructive to examine some of the changes specific to gas processing and how that segment of the industry has fared.

Given the state of the energy world, gas processing has been one of the better performers in the petroleum industry. And the segment's agility and ability to adapt to radical change will continue to keep it at the forefront of industry profitability.

As noted earlier, marketed natural gas production has declined some 26%, from about 22 1/2% trillion ft³ in 1973 to approximately 16.5 trillion ft³ in 1983. Natural gas liquids (NGL) production, however, has declined only about 10%, from 1.74 million bbl/d in 1972 to approximately 1.6 million bbl/d in 1983 (Fig. 7).

This divergence between natural gas and NGL production results from deeper extraction of NGL, increased plant efficiencies, and a significant increase in ethane production over the past 10 years. Natural gas liquids recovery per unit of gas processed has increased dramatically, from about 28 bbl/million ft³ of gas in 1973 to approximately 34 bbl in 1983an increase of about 23%.

The NGL price curve is a rough reflection of crude oil prices that are the base of energy costs throughout the world. It is interesting to note that the

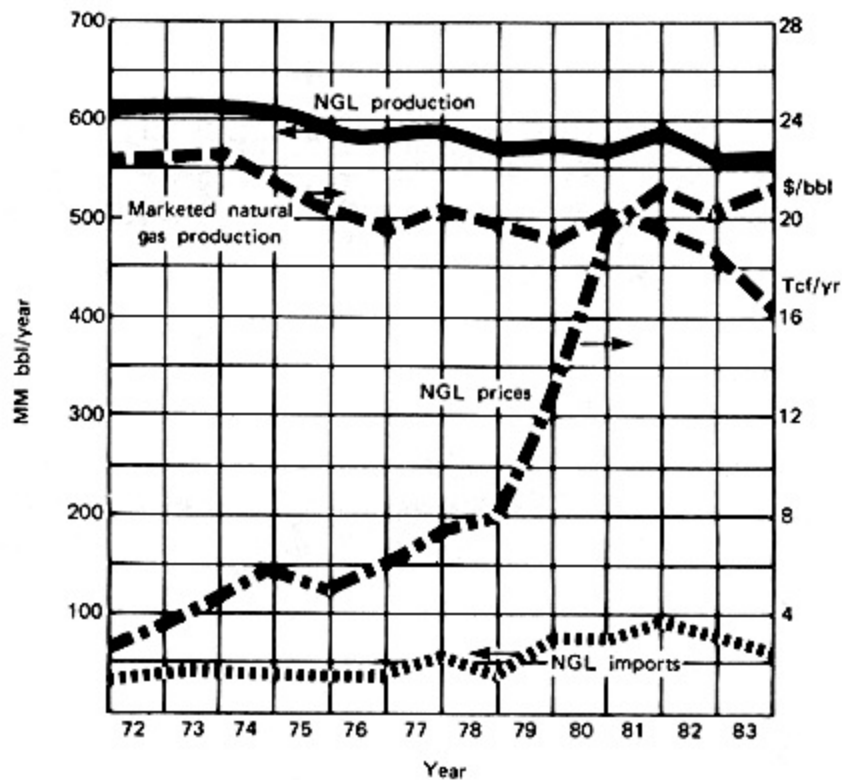


Fig. 7.

United States trends in gas processing and products.

most radical price changes in NGL history occurred during the 10 years of government price regulation, which ended in 1981.

These were three of the major changes that occurred in the gas processing industry: A declining base of natural gas feedstock, lesser decline in total NGL production, and vastly increased NGL market values over the last 5 years. Another major element, however, is the cost of gas processing's raw material, namely natural gas.

Natural gas prices are compared to NGL values over the past 10 years in Fig. 8. This graph tells us that, while NGL values have increased some 400%, the raw materials from which the liquids are extracted have increased 12 times. Economically, the gas-processing industry is being forced to run faster just to stay even.

Ten years ago, natural gas liquids were selling for slightly over \$1/million Btu, approximately \$4/bbl (Fig. 9). At that time, natural gas feedstock cost approximately 23¢/million Btu's. Simple arithmetic says that liquid values were approximately five times that of natural gas from which it was extracted.

Ten years later, NGL values have increased to an average of approximately \$5.50/million Btu. Average wellhead prices of natural gas are approximately \$2.60/MCF, resulting in a gross margin about equal to the cost of gas. In other words, NGL values have increased nearly five times. But the gross margin has decreased from about 80% of NGL market values to about 53%.

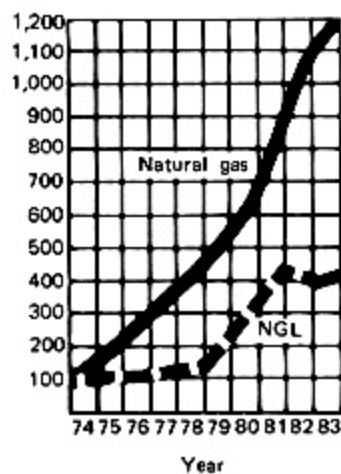


Fig. 8.
United States pricing trends
(wellhead average: 1973 = 100).

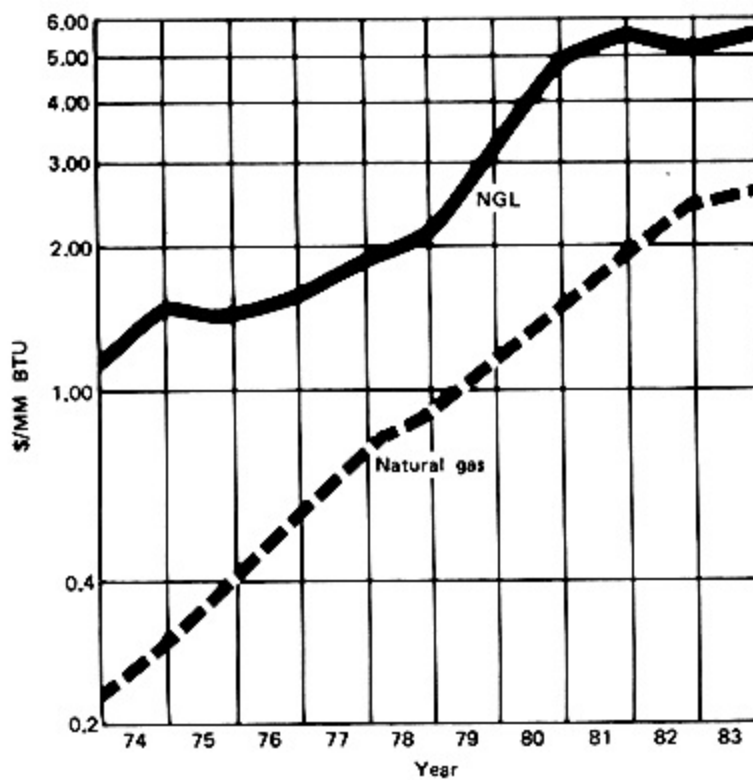


Fig. 9.
United States gas and liquid costs.

These figures, as bad as they may be for individual plant economics, may not be all bad. Many gas-processing companies are also gas producers. The total value of natural gas is still more than three times the total value of natural gas liquids at current production rates and market values.

Product Values

To complete an inspection of the gas-processing industry, it is necessary to examine each major product. In general, natural gas liquids can be divided into four major products: ethane which is used principally for petrochemical feedstock; propane which is consumed as fuel and petrochemical feedstocks; butanes, including isobutanes most of which is used in motor gasoline manufacture; and natural gasoline virtually of all which is used in motor gasoline manufacture.

Figure 10 provides a graphic view of the ups and downs of ethane over the past 4 years. This graph shows relative values of ethane and its raw material

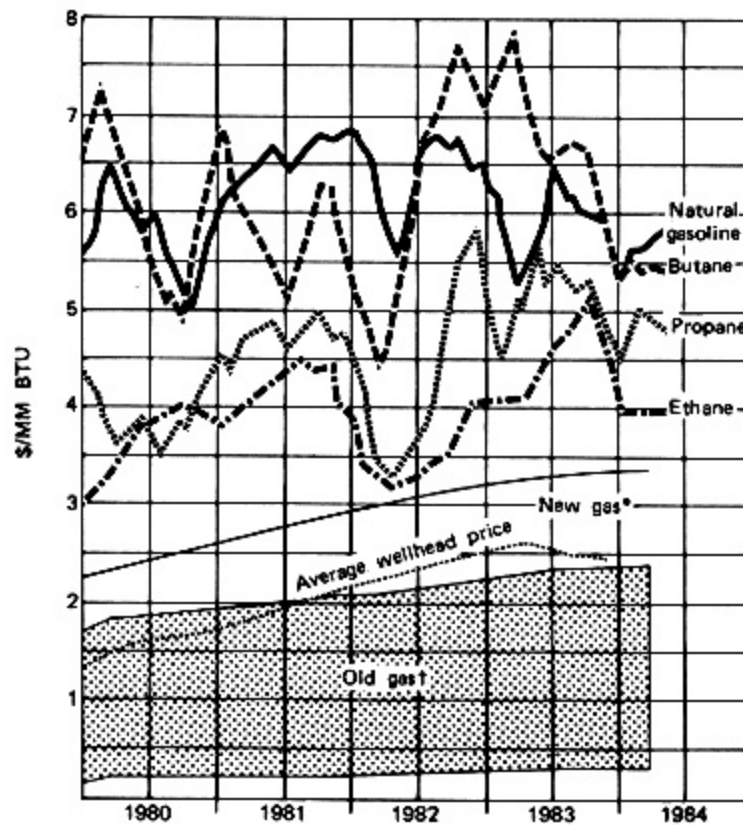


Fig. 10.
Gas plant values. (*NGPA secs 102, 103, 108, 109. +NGPA secs 104106.)

natural gas feedstock. The shaded portions of the graph show the maximum allowable NGPA prices for several categories of natural gas. Not shown are the allowable prices for Section 107 gas, since the processing of such gas is uneconomic.

This graph, perhaps as much as any other data, illustrates the rapidly changing world of gas processing. Ethane's market values have dropped as much as one-third in a 6-month period, only to rebound by two-thirds over the next 18 months. At market lows in mid-1982, ethane production from new gas was not an extremely attractive proposition.

It is interesting to note, however, that the average wellhead price of natural gas has actually been in a slow decline since early 1983. This resulted from the drop in the world price of crude oil in March 1983, at which time the natural gas industry learned the definition of the word "competition."

Until that event, natural gas was a clear economic choice over fuel oil. However at \$2425/bbl, fuel oil became a major competitor for industrial fuel markets. Natural gas lost a number of markets.

In addition, major energy loads for both oil and gas were eliminated through severe conservation measures. A similar plot of the fortunes of propane graphically illustrates the changing fortunes of the gas-processing industry where product values can drop 25% and increase over 50% in little over one year. The same plot for butane again illustrates the extreme volatility of natural gas liquids markets. Natural gasoline is relatively unexciting compared to ethane, propane, and butane.

An attempt to present a composite picture of gas-processing plant economics is made in Fig. 11. A 4-year summary of NGL production by major products illustrates the relatively level production of total NGL.

It's apparent that production of natural gasoline and heavier gas liquids is declining, principally because of the decreasing ratio of oil-well gas to leaner gas-well gas. Deeper extraction accounts for increased ethane and propane production.

Also shown are the revenue margins represented by the major NGL products. The rapid rise in natural gas raw material costs, shown as shrinkage, slowed considerably during 1983. These shrinkage costs increased by 34% in 1980, by 24% in 1981, by 23% in 1982, and slowed to an approximate 7% in 1983.

Expressed another way, shrinkage costs amounted to some 32% of the gross market value of natural gas liquids in 1980, approximately 36% in 1981, and 47% in 1982. During 1983, this cost remained constant at 47%.

Figure 11 also indicates the relative economics of major NGL products. Natural gasoline and heavier components, for example, constituted some 18% of total production in 1983, but contributed about 28% of the total perbarrel margin. Butanes comprised about 19% of total production in 1983, but contributed about 30% of total per-barrel margin.

These two major products, both of which are used in the manufacture of motor gasoline, accounted for approximately 57% of total gas plant margins of approximately 38% of total production. These fractions, however, are the shrinking portion of the total NGL barrel.

Propane production amounted to approximately 34% of NGL total, and resulted in about 30% of total margin.

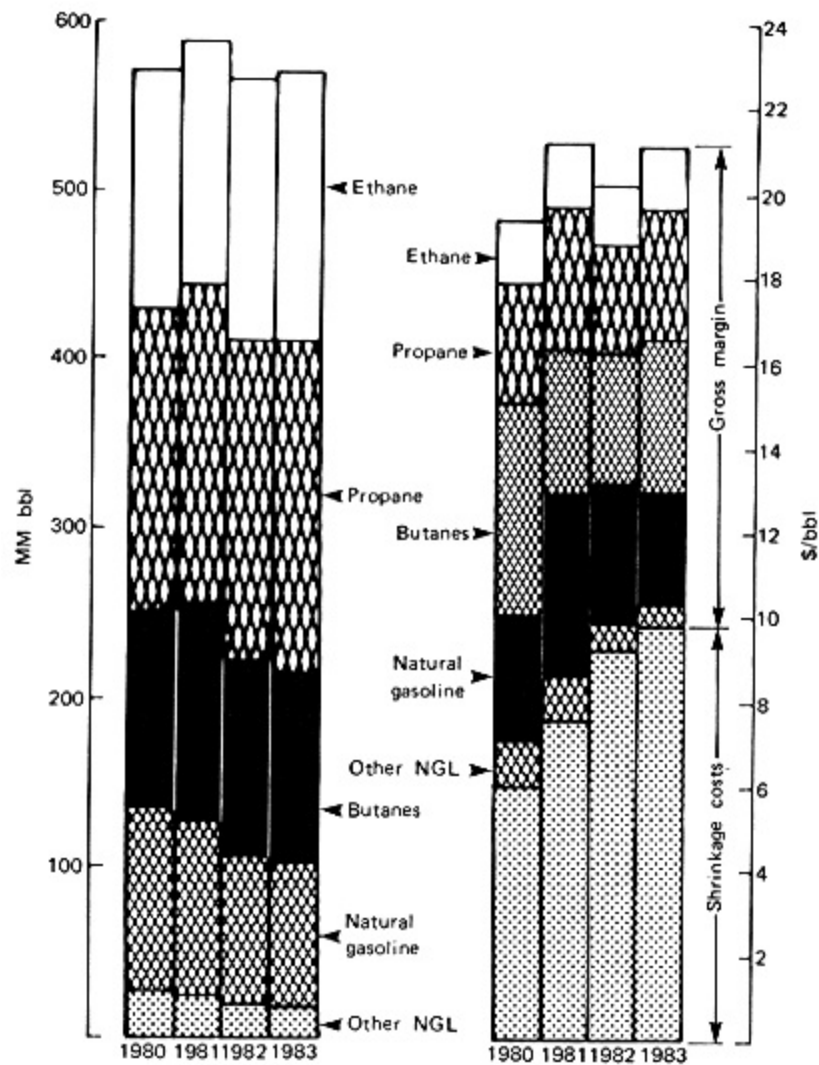


Fig. 11.
NGL production and margins.

Ethane, a major feedstock in the highly competitive petrochemical market, constituted about 28% of 1983 production, but accounted for only about 13% of total gas plant margins.

Bear in mind that these data are based on average wellhead gas prices. By definition, some processed gas is priced much higher. The processor of that gas is doing much worse. On the other hand, many plants are processing old gas. Some of this gas is still selling at very low controlled prices, \$1 or less/MCF. These processors are obviously doing much better.

One should also bear in mind, however, that much of the production included in the old gas category is declining rapidly. Incomplete data indicate that as recently as 1981, old gas made up about 60% of the mix in interstate pipelines.

By 1983, this portion had decreased to less than 50% of the mix, and continues to decline. The inevitable trend is toward higher average wellhead prices for natural gas for the simple reason that we are exhausting many old, low-priced reserves.

Changing Use

As noted earlier, natural gas liquids are used in three major markets: as feedstocks for motor gasoline, as petrochemical feedstocks, and as residential and commercial heating fuels.

Gasoline consumption, in spite of significant conservation, has declined very slowly and may even be stabilizing. This use of accounts for about 40% of total NGL production, with market values determined by demand and prices for gasoline. The other 60% of NGL production, mainly ethane and propane, is consumed as petrochemical feedstocks and heating fuels. Here, we also see evidence of the changing world of gas processing. In 1973, chemical feedstocks, including industrial fuels, accounted for about 60% of the two major uses other than gasoline manufacture; the other 40% went into residential and commercial heating.

By 1983, petrochemical feedstock use accounted for about 80% of about the same volume of ethane and propane. The residential and commercial market had declined by nearly one-half, largely because of conservation and increased use of alternate fuels, including wood.

In other words, NGL's have become basic raw materials for highly cyclical industries which are, in turn, subject to the fortunes of other highly cyclical industries, such as automobiles and housing.

Lessons to Learn

These data have been presented as a brief synopsis of recent gas processing industry history. They are presented as statistical facts to demonstrate that gas processing is indeed a changing world.

It is not enough to know history We must also learn from it. One of the lessons that is apparent, of course, is that gas processing is not an isolated segment of the petroleum industry or the world economy. It is profoundly affected by events and markets in crude oil, natural gas, petrochemicals, and by the general economic conditions of the world.

The events of the past 10 years have all but destroyed the industry's belief in the oil man's creed of the early 1970's. We have not yet been able to ascertain if alternative "conventional wisdom" exists today. Many companies and respected individuals are suggesting that the decline in energy consumption has bottomed, that excess deliverability of natural gas will disappear shortly, that worldwide economic recovery will return the vigorous growth of

the 1960s, and that market values for crude oil, the base of all energy values, will remain relatively stable into the foreseeable future.

But broad generalities are not good enough for the competitive energy world of the next 510 years. The gas processor must begin his judgment of the future with an appraisal of specifics. This will involve the following steps:

An appraisal of future crude oil prices, as determined by world politics, OPEC policy, productive capacity, and economic recovery.

A future price for residual fuel oil, derived from crude oil prices and taking into account the effects of both soft demand and probably reduced production.

The market clearing price of natural gas determined by competition from fuel oil.

The effects of partial decontrol on expiration of some price controls under the Natural Gas Policy Act of 1978, likely to be a "non-event" at the burner tip, but equally apt to result in radical dislocations in individual gas streams.

The future market for natural gas and gas liquids in the new world of energy competition.

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Alkylation

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and J. E. Gwyn

Definition

Alkylation is the introduction of an alkyl group into a molecule. As a result, the properties of the molecules are significantly altered and this forms the basis for numerous commercial processes.

Scope

By its definition, alkylation covers a wide variety of reactions. The most common of these is the formation of isoparaffins for high quality motor fuel by the reaction of isobutane with propene or butenes in the presence of a catalyst. Lesser in volume but of great importance to the petrochemical industry is the reaction of selected olefins with aromatics to form ethylbenzene, isopropylbenzene, or similar alkyl aromatics. Other reactions of interest include alkylation of phenols, aromatic amines, oxygen- or sulfur-containing compounds, and formation of organometallic compounds.

Although some alkylations may be carried out thermally at elevated pressures, the commercially important processes are conducted catalytically. Protonic acids (sulfuric acid, hydrogen fluoride, phosphoric acid) and Friedel-Crafts catalysts (aluminum chloride, boron fluoride), alkali metals, metal oxides, or salts are representative catalysts. Sulfuric acid and hydrofluoric acid predominate in paraffinic alkylation, and HCl-promoted aluminum chloride is frequently used in aromatic alkylation and ethene alkylation of isobutane.

The discussions of the theory and practice of alkylation are considered separately for isoparaffins, aromatics, and other compounds.

Paraffins by Alkylation

Background

First attempts to manufacture gasoline-range hydrocarbons from light hydrocarbons were by polymerization, primarily dimerization or trimerization, of olefins in the presence of an aluminum chloride catalyst. This approach is within the definition of alkylation but is treated separately under the more restrictive titles. Ipatieff and Grosse [70] reported in 1935 that the alkylation of hexanes with ethene is catalyzed by aluminum chloride promoted by hydrogen chloride. The first plant based on this process was placed into production in 1938.

The higher performance for gasoline quality of the isoparaffins formed from the alkylation of refinery gaseous components (particularly isobutane with butenes) relative to polymer and other gasoline components, along with the better balance of feed sources, were incentives for intensive research in this area. Numerous processes and catalysts were developed although economic factors have led to the predominance of sulfuric acid- and hydrofluoric acid-catalyzed alkylation of isobutane with butenes and propene, and sometimes pentenes, in the manufacture of isoparaffin components for gasoline. Friedel-Crafts catalysts would be required for alkylation with ethene.

Growth of the alkylation process (Fig. 1) was spurred by the need for high performance aviation gasoline during World War II during which the total capacity reached 150,000 bbl/d. Immediately after the war the process was not competitive for automotive gasoline, hence half the plants were shut down. Expansion of commercial (piston engine) aviation and the Korean War again spurred alkylation capacity to 236,000 bbl/d by the beginning of 1955.

An intensive competition in gasoline quality, the need for higher octane antiknock ratings and lower sensitivities, and the increasing cost of incremental octane rating improvements by other processes have led to the use of alkylate as a major automotive fuel component. This and the conversion of commercial aviation to jet engines have increased the use of alkylate as an automotive fuel from about 20 % of the 1956 production to its almost exclusive use for this purpose in 1973.

The value of alkylate is also reflected in the increase from 4 % of the United States petroleum refining capacity in 1960 to 6% in 1973 and a capacity increase of more than a factor of 3 since 1956. The present rate of alkylation is stabilized by the limited availability of isobutane and olefins and will be subject to increasing competition for olefins from petrochemical processes in the developing shortages of petroleum crude sources. Also the lower hydrogen content of crude oils anticipated from future sources, including shale, tar sands, and coal oils, will not favor isoparaffins without an economic means of incorporating hydrogen. Hence the emphasis on improvements has been to reduce process costs and to improve selectivity to the high performance components.

Quality of Alkylate As a Gasoline Component

The highly branched isoparaffins, with their exceptional antiknock qualities, provided alkylates with their special role, first in aviation and now in motor gasolines. The antiknock ratings of various alkylates are given in Tables 1 through 4 and the susceptibility to tetraethyl lead is shown in Fig. 2. Of particular importance is the low knock sensitivity (difference between research and motor method ratings) compared to reformat (aromatic gasoline) (Table 2). Olefinic gasolines are even more knock sensitive relative to alkylates. Although less important now, the aviation ratings show that alkylates perform well under all test engine conditions.

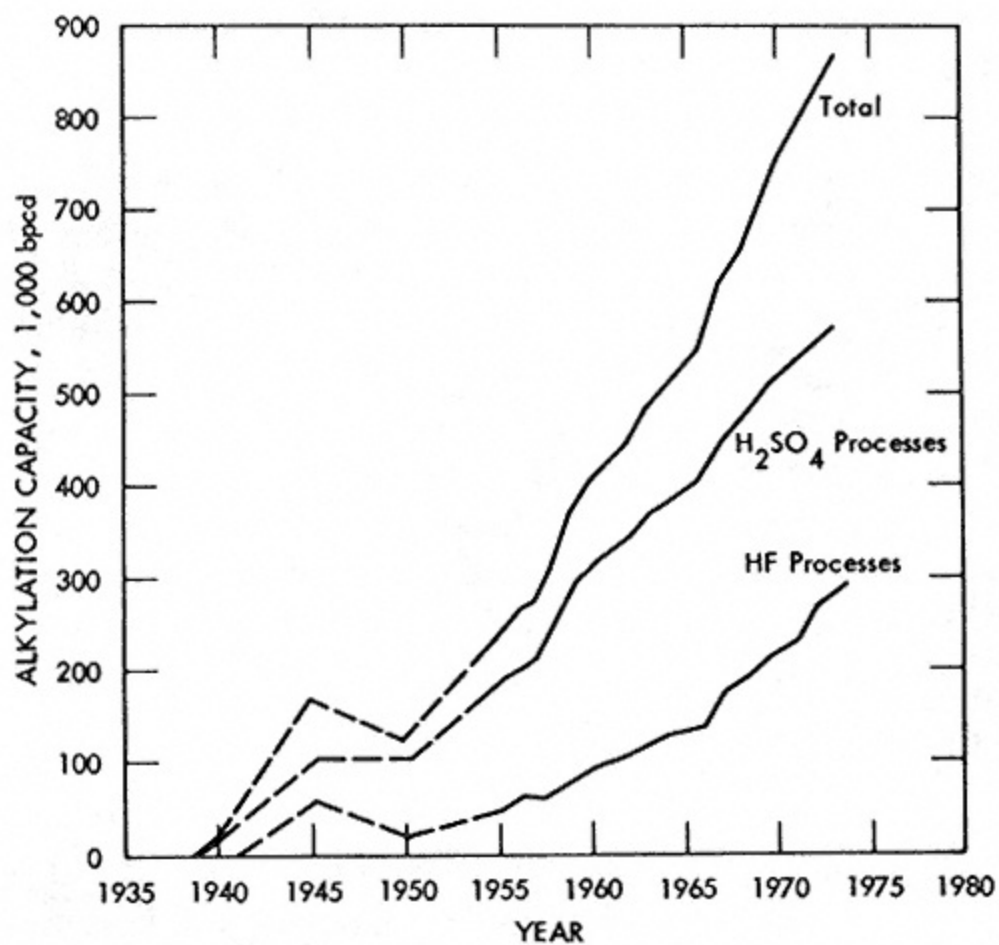


Fig. 1.
Growth of alkylation capacity in the United States [90].

TABLE 1 Unleaded Octane Numbers of Alkylates [108]

F-1 (Research)	F-2 (Motor)	Sensitivity
88.6	87	1.6
91.695	89.893	1.8
9698	9495	2.5

TABLE 2 Comparison of Leaded Octane Numbers of Alkylate and Reformate [161]

Method	3 cc TEL/gal Ratings	
	Reformate	Alkylate
F-1(Research)	103	103
F-2 (Motor)	94	104
Modified borderline		
2000 r/min	103	108
3600 r/min	103	106
Modified Uniontown	103	107

TABLE 3 Aviation and Supercharged Ratings of a Butene Alkylate [130]

Octane ratings	
F-3 + 4.6 cc TEL/gal	I.O.a + 1.9 cc TEL/gal
F-4 + 4.6 cc TEL/gal	I.O. + 3.6 cc TEL/gal
Octane numbers	
F-3 + 4.6 cc TEL/gal	110
Performance numbers	
F-3 + 4.6 cc TEL/gal	137
F-4 + 4.6 cc TEL/gal	150

aI.O. = isooctane.

TABLE 4 Blending of Butene Alkylate for Aviation Gasoline [130]

Blend composition, vol. %				
Butene alkylate	100	90	80	70
Heavy platformate	0	10	20	30
Performance numbers				
F-3 + 4.6 cc TEL/gal	137	132	127	121
F-4 + 4.6 cc TEL/gal	150	155	172	193
Blending performance nos. of platformatea				
F-3 + 4.6 cc TEL/gal		87	87	84
F-4 + 4.6 cc TEL/gal		197	257	294

aAssuming alkylate blends at its actual performance number.

The performance in blends with other gasoline components is an important factor in their acceptance in motor fuels. Isoparaffins appreciate naphthenes and olefins and blend linearly with other isoparaffins. Response with aromatic blends is mixed, but its presence reduces the tendencies for "rumbling" and other preignition-related malfunctions.

With the requirement that one grade of unleaded gasoline be marketed in the United States in 1974, the high neat octane ratings of its major components helps maintain alkylate as a major gasoline component.

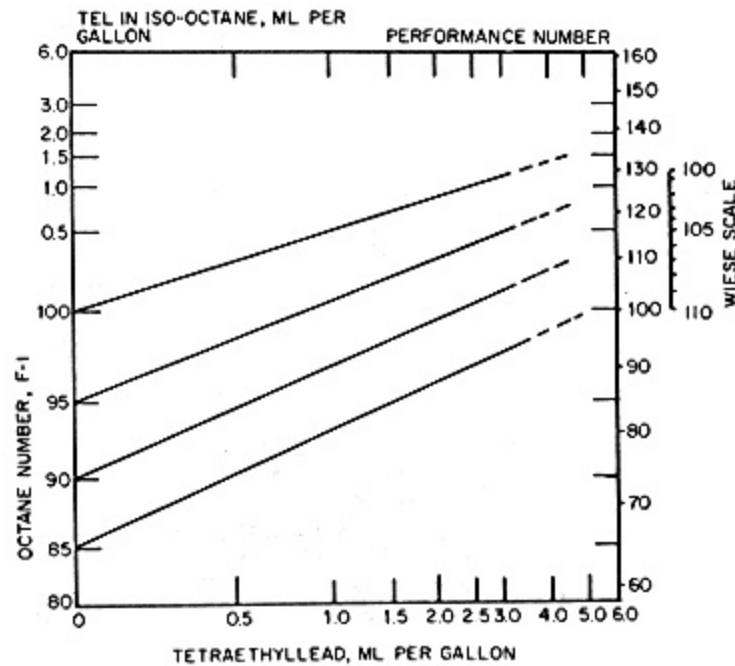


Fig. 2.
Approximate lead susceptibility of four alkylates
(research octane number) [108].

Composition of Alkylates

The development of high resolution gas chromatography and mass spectrometric analytical methods have permitted rather detailed analyses of alkylates. The quantity or absence of each paraffin may be determined as shown in Table 5. Not only do these detailed component analyses allow determination of reaction mechanism and catalyst effects, but they also allow direct prediction of stream properties.

The antiknock ratings of alkylate components are listed in Table 6. The trimethylpentanes and 2,3-dimethylbutane have the highest ratings followed by the other dimethylbutanes and the trimethylhexanes.

Thermal and Catalytic Systems

Thermal alkylation requires both high temperatures (up to 510°C) and high pressures of several hundred atmospheres. Straight chain as well as isoparaffins may thus be alkylated by olefins. The ease of thermal alkylation decreases from ethene to propene to n-butenes and least with isobutene. Side reactions include cracking and polymerization. Olefins are added slowly (to the reaction) to maintain a high paraffin to olefin ratio and thus minimize polymerization reactions.

Thermal alkylation can be induced by addition of small amounts of a

halogenated aliphatic compound or nitro compounds. These homogeneous catalysts are chain initiators and are effective between 300 and 400°C.

Catalytic alkylation occurs at mild conditions between 0 and 40°C at only sufficient pressure to maintain the hydrocarbons in the liquid phase. The catalyst exists as a separate phase, and reactants and products must transfer to and from the catalyst. Only paraffins with tertiary carbon atoms will readily undergo catalyzed alkylation. Secondary reactions include hydrogen transfer,

TABLE 5 GLC-Mass Spectrometric Component Analyses of Finished Alkylates
[146]

Component	H ₂ SO ₄ Alkylate (vol.%) ^a	HF Alkylate (vol.%) ^a
Propane	0.05	
Isobutane	0.04	0.13
n-Butane	0.92	4.87
Isopentane	8.76	5.10
n-Pentane	0.23	0.01
2,2-Dimethylbutane (DMB)		
2,3-Dimethylbutane	5.36	2.38
2-Methylpentane (MP)	1.29	0.91
3-Methylpentane	0.64	0.40
n-Hexane		
2,2-Dimethylpentane (DMP)	0.25	0.17
2,4-Dimethylpentane	3.62	1.95
2,2,3-Trimethylbutane (TMB)	0.01	
3,3-Dimethylpentane	0.01	
2,3-Dimethylpentane	2.15	1.31
2-Methylhexane (MH)	0.22	0.24
3-Methylhexane	0.14	0.12
3-Ethylpentane (EP)	0.01	0.01
2,2,4-Trimethylpentane (TMP)	24.20	38.02
n-Heptane		
2,2,3,3-Tetramethylbutane (TMB)	b	b
2,2-Dimethylhexane (DMH)	0.04	
2,4-Dimethylhexane	2.89	4.19
2,5-Dimethylhexane	4.94	3.57
2,2,3-Trimethylpentane	1.53	1.35
3,3-Dimethylpentane	b	b
2,3,4-Trimethylpentane	13.15	9.63
2,3-Dimethylhexane	3.41	4.90
4-Methylheptane (MH)		
2-Methylheptane	0.08	0.09
2,3,3-Trimethylpentane	11.47	8.14
3,4-Dimethylhexane	0.26	0.59
3-Methylheptane	0.23	0.19
2,2,5-Trimethylhexane (TMH)	7.20	3.20
	93.10	91.50

^aBasis total finished alkylate.

^bQualitatively indicated to be absent.

TABLE 6 Properties of Alkylate Components [5, 11, 43]

Antiknock Ratings						
		F-1 (Research)		F-2 (Motor)		F-4 + 4 cc
Component	bp(°C)	Clear	+3.0 cc	Clear	+3.0 cc	Perf. No.
Isopentane	27.9	92.3	(+1.0)a 108.6	90.3		142
2,3-DMB	58.0	(+0.3) 103.5		94.3	(+1.8) 112.1	205
2-MP	60.3	73.4	93.1	73.5	91.1	66
3-MP	63.3	74.5	93.4	74.3	91.3	66
2,2-DMP	79.2	92.8	(+0.4) 104.4	95.6	(+2.4) 114.0	143
2,4-DMP	80.5	83.1	96.6	83.8	99.1	83
2,3-DMP	89.8	91.1	(+0.3) 103.5	88.5	(+0.3) 103.5	140
2-MH	90.1	42.4	73.2	46.4	74.5	(90)c
3-MH	92.0	52.0	74.7	55.8	81.0	(80)c
2,2,4-TMP	99.2	100.0	(+3.0) 115.5	100.0	(+3.0) 115.5	154
2,5-DMH	109.1	55.2	81.6	55.7	82.9	44
2,4-DMH	109.4	65.2	87.3	69.9	89.0	(80)c
2,2,3-TMP	109.8	(+1.2) 109.6		99.9	(+2.0) 112.8	238
2,3,4-TMP	113.7	(+0.2) 102.5		95.9	(+0.7) 106.7	193
2,3,3-TMP	114.8	(+0.6) 106.0		99.4	(+2.0) 112.8	225
2,3-DMH	115.6	71.3	91.7	78.9	93.7	102
2,2,5-TMH	124.1	91b		88b		(150)c
2,3,5-TMH	131.4	81b		78b		(120)c
Isoparaffins	126140			(75.7)c		(100)c
Isoparaffins	140159			(35)c		(100)c
Isoparaffins	159178					(60)c
Isoparaffins	>213					(60)

^aFor octane numbers above 100, numbers in parenthesis are isooctane + cc TEL/gal. Numbers are octane rating on Wiese scale.

^bBlending octane numbers.

^cEstimated.

destructive alkylation, polymerization, and formation of esters and catalyst complexes.

Reactions

Theory and Thermodynamics

In alkylation as commonly practiced, the reactants are limited to a few olefins, usually butenes, and isobutane. However, there are numerous product components in addition to the primary products which result from a number of secondary reactions. These same components are produced from different olefins but in greatly different proportions. The absence of specific isomers and the unexpected presence of others have been used to determine prohibited and favored reaction schemes. The current state of knowledge has resulted from extensive research with different olefins, isoparaffins, catalysts, reaction con-

TABLE 7 Alkylation of Isobutane with Butenes and HF Catalyst at Conditions Favoring Primary Product and Favoring Thermodynamic Equilibrium [50, 127]

Olefin	Favoring Primary Product			Favoring Thermodynamic Equilibrium			Equilibrium Composition
	1-Butene	2-Butene	Isobutene	1-Butene	2-Butene	Isobutene	
Temperature (°C)	-10	-10	-11	49	49	47	41
Contact time (min)	5	5	5	250	250	259	
Octanes (%)							
2,2,4-TMP	14.0	38.9	74.8	32.5	37.0	39.7	29.6
2,4-DMH	5.2	4.5	8.4	43.6	33.9	31.5	56.8
2,3,4-TMP	21.3	39.1	16.8	12.0	11.9	17.8	4.5
2,3,3-TMP		14.2			8.3	5.0	3.4
2,3-DMH	59.5	3.3		11.9	8.9	6.0	5.7
C8 in C5 + alkylate (wt.%)	63.1	80.4	64.5	39.2	35.7	41.2	

ditions, alkylation of polymers, radioisotopes, and disproportionation reactions.

Primary products are determined by operation at conditions that minimize isomerization and other side reactions, generally low temperatures and short contact times. Isobutane alkylated with 1-butene forms 2,3-dimethylhexane (2,3-DMH) as the primary product, with 2-butene forms 2,2,4-trimethylpentane (2,2,4-TMP) and 2,3,4-trimethylpentane (2,3,4-TMP) in about equal amounts, and with isobutene forms 2,2,4-TMP (Table 7). Primary products of alkylation with ethene and propene are 2,3-dimethylbutane (2,3-DMB) and 2,3-dimethylpentane (2,3-DMP), respectively (Table 8).

Reactions at high temperatures and long contact times favor thermodynamic equilibrium, Table 7, and result in large quantities of the thermodynamically favored 2,4-DMH, but the compositions do not closely approach equilibrium composition of all octanes. Secondary products of different carbon numbers always formed include isopentane, 2,3-DMB, and 2,2,5-trimethyl-

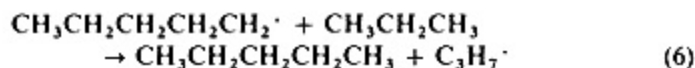
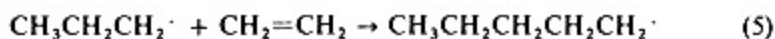
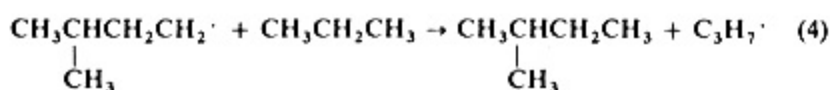
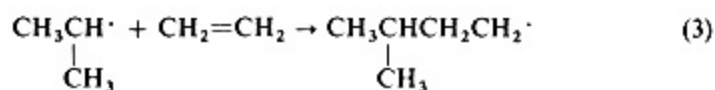
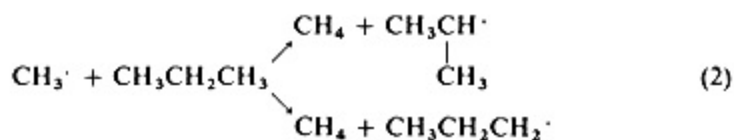
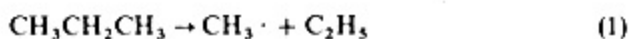
TABLE 8 Alkylation of Isobutane with Ethene and Propene Using AlBr₃ Catalyst at Conditions Favoring Primary Products [50]

Olefin	Ethene		Propene	
Temperature (°C)	50		17	
Residence time (min)	225		4	
Wt.% in C5C8 alkylate	2,2-DMB	4.0	2,4-DMP	4.6
	2,3-DMB	78.9	2,3-DMP	78.3
	Other	17.1	Other	17.1
		100.0		100.0

hexane (2,2,5-TMH). Saturated products of the same carbon number as the olefin and of twice the carbon number of the feed isoparaffin are also formed.

Thermal Alkylation-Free Radical Reactions

Thermal alkylation is reported to occur by a free radical chain reaction as indicated below [75]. For alkylation of propane with ethene:



The radicals formed via Reactions (4) and (6) perpetuate the cycle through Reactions (3) and (5). Isopropyl radicals are formed preferentially to n-propyl since hydrogen attached to a secondary carbon is more readily abstracted than hydrogen attached to primary carbon atoms. Therefore, more isopentane than n-pentane is formed. Olefins are also formed by polymerization, and other secondary products include hexanes and heptanes.

The reaction of propane with propene results in product yields of 17.7 and 5.4% of the expected products 2-methylpentane and n-hexane, respectively, but also an unexpected 18.0% of 2,3-DMB [136]. This might be explained by the combination of two isopropyl radicals. The presence of isopentane, n-pentane, heptanes, and olefins indicates that cracking and polymerization reactions also occur.

Isobutane does not react readily with isobutene (liquid product was only 35 wt.% of the isobutene at 8000 lb/in² and at 486°C [136]). The liquids were about 1/3 octanes and 1/3 octenes.

In induced thermal alkylation the products are the same as those in thermal alkylation. The homogeneous catalysts appear to be chain initiators and their activities appear to be related to their thermal instability.

Catalytic Alkylation

Catalysts

Friedel-Crafts catalyst such as aluminum chloride promoted by hydrogen chloride causes alkylation of isobutane with olefins, other than ethene, to occur at temperatures as low as -35°C . With ethene, room temperatures or higher are required. At room temperature with the other olefins, cracking and other side reactions result in a low yield of the primary products. There are some reports that the secondary reactions may be suppressed by complexed catalyst modifiers.

However, except for ethene, which forms stable esters with these acids, sulfuric acid or hydrofluoric acid are used almost universally for alkylation of isobutane. Long acid life and convenient liquid state are responsible for their acceptance.

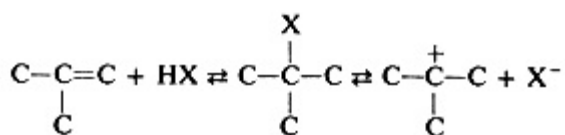
Carbonium Ion Mechanism

Reaction occurs with both catalysts through a carbonium ion mechanism. Only isoparaffins containing a tertiary carbon atom undergo catalytic alkylation with olefins. The primary product does not have the structure of simple addition of hydrogen and an alkyl group from the isoparaffin across the double bond of the olefin. The alkylation reaction obviously involves structural rearrangement. The carbonium ion mechanism as proposed by Whitmore [167, 168] has been applied to alkylation by Birch and Dunstan [18], Schmerling [135, 137, 138], Bartlett [16], and others.

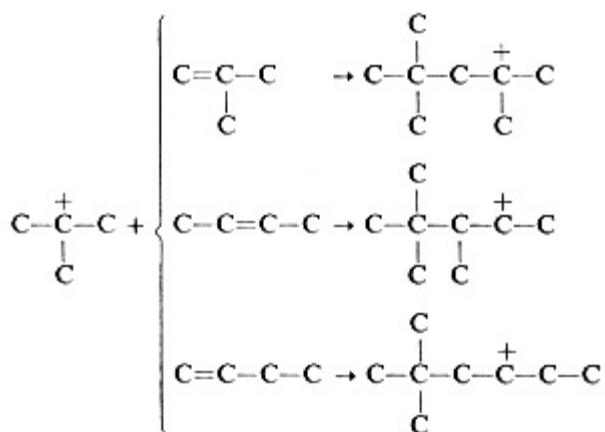
Reaction Scheme

A molecule containing a carbon atom which has a deficit of two electrons in its outer shell is known as a carbonium ion. It has a positive charge and is paired with an anion of the catalyst. The anion is ever-present but frequently in reaction notation only the carbonium ion is shown for convenience. The stability of carbonium ions is in the order of tertiary > secondary > primary, and the tertiary are the only ones stable enough to undergo saturation by reaction with an isoparaffin. Other carbonium ions rapidly isomerize to a tertiary ion. The reaction scheme may be summarized as follows [26] (X is OSO_3H , F, or HAlCl_4):

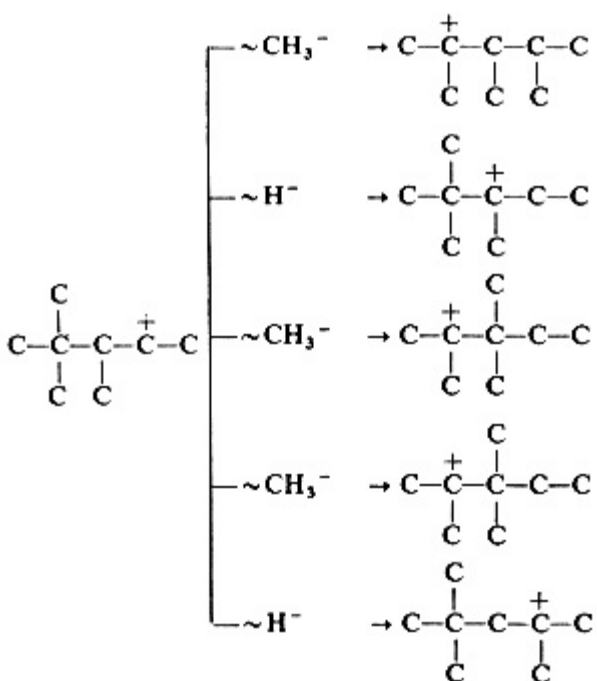
1. Proton addition to olefin:



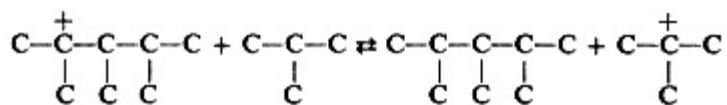
2. Carbonium ion addition to olefin:



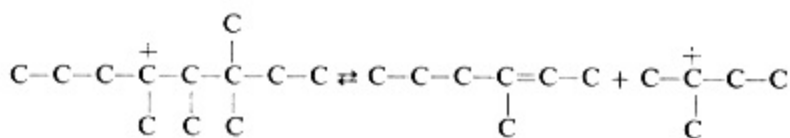
3. Isomerization via hydride and methyl shifts:



4. Hydride-ion transfer:



5. Cracking:



Reactions of Type 1 represent initiation reactions and require some induction time to generate an effective level of ions. At steady state these reactions are insignificant to the others. For isobutene the tertiary carbonium ion is formed directly by Reaction 1. For other olefins the carbonium ions formed may in turn form tertiary butyl ions through isomerization reactions or hydride ion transfer with isobutane. Thus initiation reactions with linear olefins are slower than those with branched olefins [157].

The formation of primary product proceeds by the addition reaction of olefin and t-butyl carbonium ion given by Reaction 2. This carbonium ion may isomerize to a more stable form by hydride and methyl shifts shown by Reaction 3. Saturation of the final tertiary carbonium ion by hydride ion transfer from isobutane is shown by Reaction 4. The primary isoparaffin alkylates are thus formed and the reaction sequence is perpetuated by the formation of another t-butyl carbonium ion.

The cracking Reaction 5 is listed separately from the reverse Reaction 2 in that isomerization may occur before cracking and results in a different olefin and carbonium ion than in Reaction 2. Intramolecular hydride and methyl shifts are postulated to occur normally by transfer from carbons adjacent to the carbon containing the positive charge. However, a methyl shift from the second to the fourth carbon is postulated to explain the observation of 2,3,4-TMP as the primary product of alkylation with 2-butene.

Since only tertiary ions readily abstract hydride ions from isobutane, 2,4- and 2,3-DMP are the primary alkylates from propene. Under conditions minimizing isomerization the carbonium ion from isobutene addition is saturated directly to 2,2,4-TMP (Table 7). However, with 2-butene addition the carbonium ion must first undergo hydride or methyl shifts to form a tertiary ion. Thus 2,2,4-TMP and 2,3,4-TMP (as mentioned above) are formed. With 1-butene a methyl shift is required to form a tertiary ion, and hence 2,3-DMH is the primary product.

Secondary Reactions

The complex yield distributions from alkylation attest to the difficulty of obtaining only primary products. Reactions leading to secondary products are implied in Reactions 2 through 5. These are classified as polymerization, isomerization, self-alkylation, and disproportionation, respectively.

Polymerization results from the addition of another olefinic group to the carbonium ion formed in the primary reaction. For alkylation with butenes this results in C₁₂ and C₁₆ ions. Cracking of carbonium ions increases with carbon number and results in alkylate

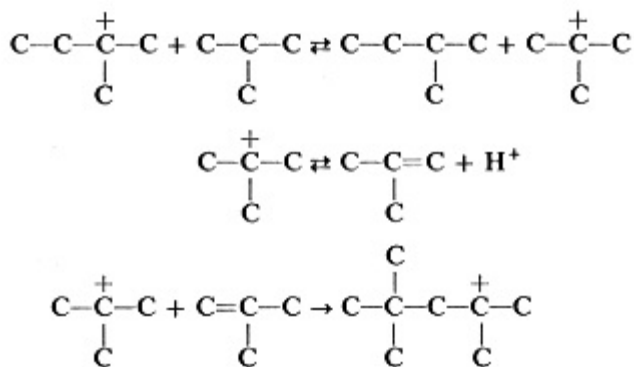
products other than octane.

Isomerization of the primary tertiary carbonium ions results in a wider distribution of components of the same carbon number. Thermodynamic equilibrium is favored for those isomers that can be produced through permissible reaction paths.

Trimethylpentanes can be obtained by the self-alkylation (hydrogen transfer) of isobutane even when propene or pentenes are alkylated. The overall reaction is



The reaction scheme for pentenes, for example, is



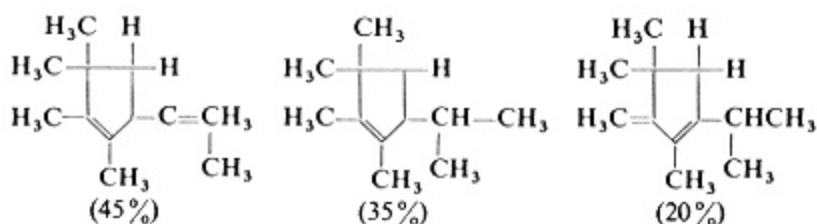
A saturated paraffin of the same carbon number as the olefin is obtained along with the trimethylpentane. Since isobutane is generally in short supply, self-alkylation is not considered to be a desirable reaction. Hydrogen transfer alkylation of propene occurs in hydrofluoric acid but not with sulfuric acid.

Disproportionation results in the disappearance of some alkylate isoparaffins before the hydrocarbons leave the reactor. These isoparaffins may reenter the reaction scheme by a hydride ion transfer reaction such as the reverse of Reaction 4. They then undergo degradation by the other secondary reaction, i.e., isomerization, polymerization, and cracking. Hofman [60] found that 2,2,4-trimethylpentyl cations in sulfuric acid isomerize to the other trimethylpentyl isomers and closely approach equilibrium among these isomers. However, dimethylhexanes, also found in appreciable quantities, were formed from cracking and alkylation sequences rather than by isomerization.

Relative disproportionation rates have been measured by contacting specific isoparaffins with alkylation acids (since olefins were not present, these tests were under carbonium ion deficient conditions). 2,2,4-TMP, 2,2,3-TMP, 2,3,4-TMP, 2,2,5-TMH, and 2,3-DMB break down in some degree to form higher and lower molecular weight isoparaffins. 2,3,4-TMP and 2,2,4-TMP disproportionate most readily, and 2,3-DMB the least. Isopentane, 2,2-DMB, and 2,2,3-TMB do not disproportionate. In the presence of t-butyl fluoride and boron fluoride, 2,2,4-TMP is inert toward destructive alkylation of isobutane and results in a large yield of this octane.

Catalyst Complexes

Acid catalysts in isoparaffin olefin alkylation become exhausted primarily as a result of a buildup of salts of stable cyclopentenyl cations [23]. In a pilot plant reactor where acid was depleted from 98 to 88 wt.% H_2SO_4 by isobutane-isobutene alkylation, the water content increased from 0.6 to 2.8 wt.% while the soluble (polymer) hydrocarbons increased from 0 to 6.5 wt.%. Upon slow neutralization with intense mixing a black carbonaceous substance and a separate light yellow-orange oil, which darkens on standing, is obtained. This "conjunct polymer" is 82% in the $\text{C}_{10}\text{C}_{16}$ range and 97% in the $\text{C}_{10}\text{C}_{20}$ range. The ring skeletons are highly substituted and the relative ring structure distribution is given by:



Red or red-brown complexes are also obtained when aluminum chloride or hydrofluoric acid catalysts are used.

Methyl cyclopentane reacts more rapidly with isobutene than does isobutane. Kennedy [83] illustrated a number of reactions in which cyclopentyl ions are formed and hydride ions are abstracted to form unsaturated rings. These may undergo reaction with carbonium ions and methyl shifts to form complex cyclopentanes.

Ester Formation

Alkyl esters are obtained when conditions are unfavorable for hydrogen exchange with the isoparaffin. Ethene forms stable esters with H_2SO_4 or HF.

Thermodynamics, Olefin, and Isoparaffin

The principle octane isomers (2,4-DMH, 2,3-DMH, 2,2,4-TMP, 2,3,4-TMP, and 2,3,3-TMP) approach equilibrium relative to each other at relatively high temperatures and long contact times; however, at normal alkylation conditions their equilibrium concentrations would total only about 25%. The methylheptanes, 2,5-DMH, and 2,2-DMH, which do not exist in appreciable quantities, would have equilibrium concentrations totaling about 60%.

A wider variety of isoalkane-olefin alkylate compositions are listed in Table 9. The similarities between 2-butene and 1-butene alkylates are explained by the rapid isomerization (in sulfuric acid) via the secondary butyl ester, with 2-butene being the preferred isomer. Isomerization is less in hydrofluoric acid

TABLE 9 Alkylation of Various Olefin-Isoparaffin Combinations with 96 wt.% H2SO4 (C.P.) at 7°C in a Well-Mixed Flow Reactor								
Isoparaffin Feed		Isobutane						
Olefin Feed	Propene ^a	Isobutene	2-Butene	1-Butene	2-Methyl-2-butene	2-Methyl-1-butene	2-Pentene	Propene
Feed, vol. %								
Olefin	15.9	15.8	16.7	14.9	14.8	16.2	17.2	14.4
Isoparaffin	77.0 ^d	80.5 ^d	80.3 ^d	78.9 ^d	78.6 ^d	81.3 ^d	80.6 ^d	81.4 ^e
n-Paraffins, C3C5	7.1	3.7	3.0	6.2	6.6	2.5	2.2	4.1
Reactor hydrocarbon, b vol. %								
Product ^c	30.2	25.0	29.8	29.6	40.6	36.9	31.7	36.3
Isoparaffin (feed type)	62.9 ^d	70.3 ^d	65.3 ^d	64.5 ^d	53.9 ^d	58.6 ^d	64.6 ^d	63.7 ^e
n-Paraffin, C3C5	6.9	4.7	4.9	5.9	5.5	4.5	3.7	7.0
Product, c vol. %								
Isobutane								7.04
Isopentane	3.79	10.01	4.16	4.66	25.27	28.22	19.26	
2,3-Dimethylbutane + methylpentane	4.24	5.21	4.58	4.44	5.35	6.44	1.85	10.24
2,4-Dimethylpentane	20.75	3.85	2.37	2.61	2.60	2.15	0.82	2.27
2,3-Dimethylpentane	50.36	2.57	1.38	1.45	1.65	1.55	0.55	4.13
2,2,4-Trimethylpentane	4.43	28.67	30.64	30.49	16.53	17.49	9.84	None
Dimethylhexane (DMH)	1.70	9.53	9.02	11.03	6.74	7.33	2.80	53.73 ^f
2,3,3- + 2,3,4-Trimethylpentane	3.70	23.11	41.55	39.08	14.71	14.61	7.91	None
2,2,5-Trimethylhexane	0.87	4.88	1.88	1.77	12.43	9.70	46.55	3.33
Other C ₉ ^h	0.42	1.69	0.53	0.69	3.51	2.86	8.10	3.84
C ₁₀ ^h	5.25	2.49	0.67	0.56	5.43	5.15	1.53	6.72
C ₁₁ ^h	3.73	2.12	0.66	0.65	1.94	1.69	0.10	5.79
C ₁₂ ^h	0.44	5.60	2.55	2.49	3.09	2.37	0.30	2.62
C ₁₃ ^h	0.32	0.28		0.08	0.74	0.44	0.40	0.29

a47 vol.% acid in emulsion; 0.22 olefin (liquid-hourly) space velocity [26].
bProduct analyses by GLC.
cC4-and-heavier product exclusive of n-paraffins and feed-type isoparaffin.
dIsobutane.
eIsopentane.
fDimethylhexanes: 2,5-DMH, 18.9; 2,4-DMH, 30.7; 2,3-DMH, 43.6; 3,4-DMH, 6.8.
g98 wt.% H2SO4.
hEstimated from boiling point range.

than is sulfuric acid, and hence produces more 2,2,4-TMP and less 2,3,3-TMP and 2,3,4-TMP.

Alkylates of isopentane are similar to those of isobutane but one carbon number greater, e.g., trimethylhexane rather than trimethylpentanes. Isobutene with isopentane tends to disproportionate into hexanes and decanes.

Properties of Alkylation Catalysts

The protonic acids, sulfuric acid and hydrogen fluoride, are preferred over halides of the Friedel-Crafts type for commercial alkylation since, as liquids, they are more readily handled. Also, since they catalyze fewer secondary reactions, the yield structure and catalyst life is better for the protonic acids. However, Friedel-Crafts catalysts may offer more potential for modifying the alkylation reaction through use of catalyst complexes.

Acidity, Isobutane Solubility

The properties of the two common protonic acids are given in Table 10. Those properties which most directly affect their catalytic functions are their acidity and the solubility of isobutane in the acid. The ease of producing carbonium ions from olefinic molecules via proton transfer is related to the Hammett acidity function. Sulfuric acid has greater acidities than hydrogen fluoride over the commercial range of acid concentrations, and both have their acidities reduced by water (Fig. 3). Acidities are reduced to a much lesser extent by

TABLE 10 Catalyst Properties [59, 67, 68, 117, 149]

	HF		H ₂ SO ₄	
Molecular weight	20.01		98.08	
Boiling point (°C)	19.4		290	
Freezing point (°C)	-82.8		10	
98% acid			3	
Specific gravity	0.99		1.84	
Viscosity (cP)	0.256	(0°C)	33	(15°C)
Surface tension (dyn/cm)	8.1	(27°C)	55	(20°C)
Specific heat (Btu/lb/F)	0.83	(-1°C)	0.33	(20°C)
Hammett acidity (-H ₀) at 25°C	10.0		11.1	
98% acid at 25°C	8.9		9.4	
Dielectric constant	84	(0°C)	114	(20°C)
Liquid solubility (wt.%)				
i-C ₄ H ₁₀ in 100% acid at 27°C	2.7			
i-C ₄ H ₁₀ in 99.5% acid at 13°C			0.10	
HF in i-C ₄ H ₁₀ at 27°C	0.44			
HF in C ₃ H ₈ at 27°C	0.90			

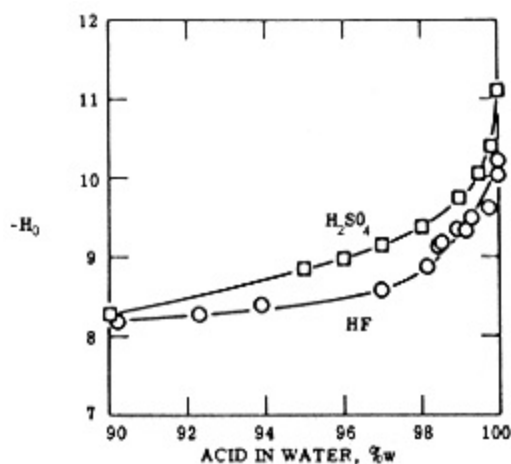


Fig. 3.

Hammett acidity function, H_0 , of sulfuric and hydrofluoric acids in water at 25°C [68, 117].

organic diluents. Both the solubility of isobutane in acid and of acid in isoparaffins are higher for hydrofluoric acid.

Both acidity and solubility of isobutane control the concentrations and average life of carbonium ions. Isomerization and polymerization reactions are favored by strong acidity and low isobutane solubility; thus the selectivity to primary products is improved by increased isobutane solubility and reduced acidity. Although the organic diluents tend to respond in this direction and there is an optimum acid strength, the ability to alter yield favorably by adjusting acid composition has been limited.

In this respect hydrofluoric acid produces alkylates with more 2,2,4-TMP than does sulfuric acid. In addition, shorter contact times (high space velocities) are used with hydrofluoric acid due to the higher hydride ion transfer rates. Also, higher temperatures (to 38°C) are permitted with hydrofluoric acid. Higher temperatures for sulfuric acid result in a much greater formation of stable acid soluble compounds and increased secondary reactions which give short acid life and poor alkylate quality.

Physical Properties

Other differences in physical properties between hydrofluoric and sulfuric acid which affect the design of reaction systems are given in Table 10. HF has a low boiling point which allows spent acid to be regenerated by simple distillation. The high freezing point of sulfuric acid sets a limit to which it can be cooled ($\sim 40^\circ\text{F}$) to improve yield structure. The high viscosity, surface tension, and density along with low isobutane solubility requires much more intensive mixing of the hydrocarbon/acid mix with sulfuric acid than with HF. In fact, HF

units have been operated with no dispersive mixing other than that caused by rising hydrocarbon droplets.

Decline of Acid

When acid degrades to the point where it cannot maintain sufficient carbonium ion concentration, then runaway acid decline occurs due to excessive conjunct polymer formation. Water decreases acid activity several times more rapidly than does organic diluent. Indeed, organic material is reported to increase isobutane solubility and improve product selectivity. A lower level of titratable acidity can be tolerated in the dropout acid if the water content of the fresh, makeup acid is kept low. Charge acid strengths in the region of 98 to 100 wt.% H_2SO_4 and 99.5 wt.% HF titratable acidity are reported to give optimum results.

Catalyst Regeneration

While HF can be regenerated by distillation, spent sulfuric acid is generally used for other purposes, such as treating, or is reprocessed off-site by the sulfuric acid manufacturers. Regeneration of this acid and of spent sulfuric acid from chemical plants usually involves partial burning to remove hydrocarbons and then refortification with oleum. The regenerated acid, black because of remaining carbonaceous material, has been found to be an excellent alkylation acid.

The cost of other acid and pollution restrictions have caused increasing interest in on-site regeneration. Numerous schemes for regeneration of sulfuric acid are found in the patent literature. They include (1) crystallization of the acid by cooling, (2) reactions with olefins to form alkyl sulfates and isoparaffins, (3) extraction with propane, (4) filtration, (5) high temperature treatment, and (6) electrolysis. For example, propene is reacted with the spent acid to form dipropyl sulfate. This is then extracted with isobutane and treated with sulfuric acid. The sludge is withdrawn and then retreated with sulfuric acid and butene to form alkanes. This suggests that at some point where the sludge material is eliminated the sulfate mix may be returned to the alkylation reactor to form alkylate and an effective catalyst.

Reaction Rates

The reactor mechanics of the sulfuric acid system is the more interesting of the two acids because in commercial units isobutane transfer is rate limiting to some degree. Sulfuric acid alkylation has been reported in terms of rate constants and rate limiting mechanisms by Jernigan, Gwyn, and Claridge [76], Sprow [153], and Langley [92].

The reaction scheme for butene alkylation as discussed before was summarized by Jernigan et al. (Fig. 4). Accordingly, all alkylate is produced by

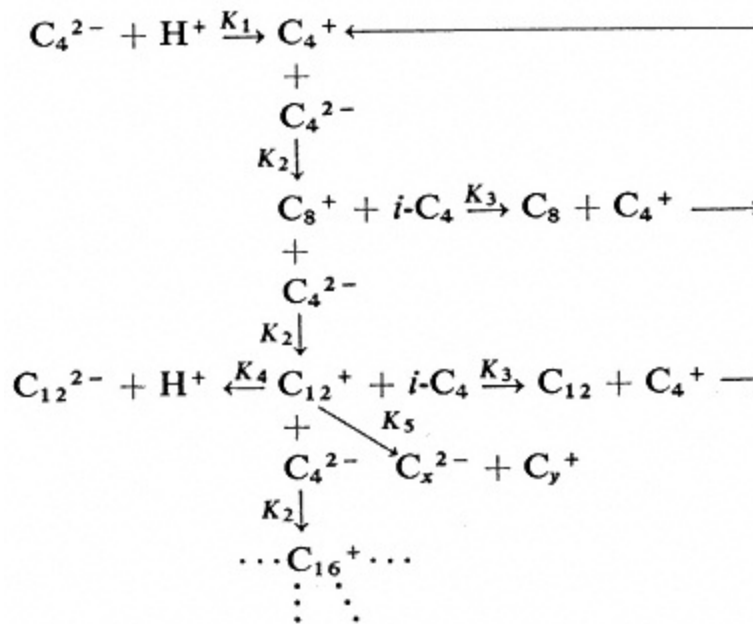


Fig. 4.

Butene/isobutane alkylation reaction mechanism [76].

Where C_4^{2-} = butene, C_4^+ = isobutyl carbonium ion,

H^+ = proton from acid, $i-C_4$ = isobutane,

C_x^{2-} = olefin of carbon number x ,

C_y^+ = carbonium ion of carbon number y , and

C_n = saturate of carbon number n .

way of C_8 carbonium ions. In large excess of isobutane the C_8 carbonium ions should be preferentially saturated by Reaction 3 to produce C_8 alkylates and isobutyl carbonium ions. This occurs at low olefin space velocities and in large excesses of isobutane. Octanes are then considered to be the primary product. The measure of quality used in the model development was the ratio of primary to nonprimary alkylate. Thus

$$C_8/\text{other} = \frac{K_3 B_a}{K_2 E_a}$$

where B_a = concentration of isobutane in the acid phase

E_a = concentration of olefin the acid phase

In the absence of mass transfer limitations, this ratio was developed in terms of a severity factor as

$$C_8/\text{other} = K_p J$$

where $J = B_h/S^{1/2}$

B_h = isobutane content in the hydrocarbon phase

S= olefin space velocity

Kr = ratio of rate constants

Where mass transfer is limiting, this became

$$C_{g/\text{other}} = \frac{K_r B_h}{S^{1/2} + \frac{K_r K_I S}{K_g K_m A}}$$

where K_I = fraction of carbonium ions which are not C_8^+

$K_m A$ = mass transfer coefficient

K_B = partition coefficient of isobutane between acid and hydrocarbon

Jernigan et al. developed the transfer term in terms of emulsion quality (fraction of hydrocarbon occurring as a stable emulsion), Fig. 5. (H_e is the fraction of hydrocarbon in the emulsion phase; H and V are total volume of hydrocarbon and acid, respectively.)

Sprow further developed the interfacial area in terms of mixing in a stirred reactor which under mass transfer limiting conditions reduced to

$$C_{8/other} = K_{10} \frac{B_s N^{3/4} (1 - V)}{S}$$

where N = stirrer speed

V = volume fraction acid phase

K_{10} = proportionality constant

The relation is shown in Fig. 6.

Langley [92] developed a model for alkylation of isobutane with propylene under constant mixing conditions. The rate constants for each reaction are listed in Table 11. The resulting first-order rate constants were in the range of 2×10^4 to 1×10^6 s⁻¹ and second order were 2×10^5 to 1×10^{18} cc/g·mol·s. Activation energies are small, and those involving i-C₄ were assumed to be zero due to transfer limitations.

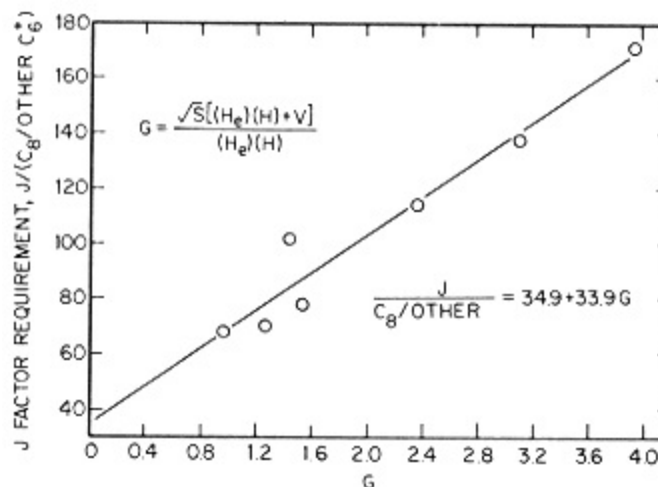


Fig. 5.

Effect of isobutane mass transfer limitation on J factor

requirement [76].

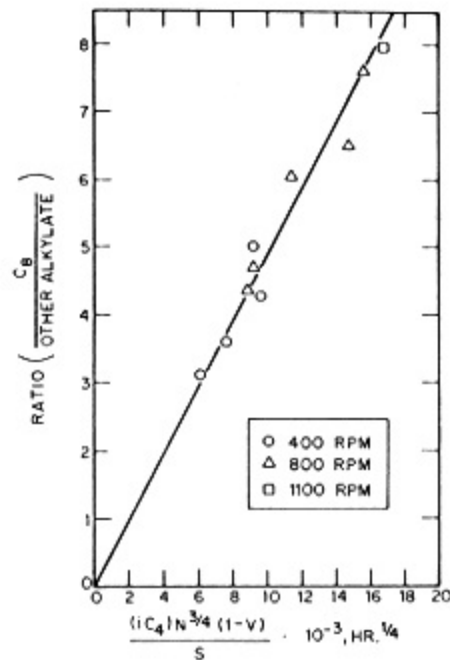


Fig. 6.
Alkylate quality correlation based on
strong mass transfer limitations [153].

Technical Factors

In addition to the reactor design and choice of catalysts, a number of control variables affect the yield and quality of alkylates. These include acid strength, reaction temperature, isobutane and olefin concentrations and feed rates, composition of feeds, contaminants, and emulsion quality. Process effects are similar for HF and H₂SO₄ but requirements for the sulfuric acid process are more severe. Significant differences are discussed below.

Acid Strength and Consumption

The maximum sulfuric acid strength is usually limited to 99% because of the reaction of SO₃ with isobutane, and the minimum is limited by runaway dilution in the region of 85 to 88 wt.% H₂SO₄. Both yield and quality experience maxima in the region of 95 to 97 wt.% H₂SO₄ depending on conditions (Fig. 7). Below this optimum, yield and quality decrease steadily with decreasing strength. The desired dropout strength is a balance between alkylate yield and acid life. An overall better performance is obtained by staging the acid between three or four reactors rather than operating the entire system at dropout strength.

For a given dropout strength, acid consumption is reduced by those

TABLE 11 Results of the Least-Square Fits of the Rate Constants over the Range -3 to 14°C and with a 95% H₂SO₄ Catalyst [92]

Reaction Rate	Rate Law	Frequency Factor ^a	Activation Energy ^b
Initiation			
$C_3^{2-} + HX \xrightarrow{k_1} C_3 + X^-$	kAB	1.01×10^7	2.35
$C_3 + X^- + i-C_4 \xrightarrow{k_2} C_3 + i-C_4 + X^-$	kAB	2.07×10^{11}	0.0
Primary			
$i-C_4 + X^- + C_2^{2-} \xrightarrow{k_{11}} i-C_7 + X^-$	kAB	1.99×10^{17}	2.36
$i-C_7 + X^- + i-C_4 \xrightarrow{k_5} i-C_{10} + i-C_4 + X^-$	kAB	4.20×10^{10}	0.0
Self-alkylation			
$i-C_4 + X^- \xrightarrow{k_9} i-C_4^{2-} + HX$	kA	3.92×10^4	0.40
$i-C_4 + X^- + i-C_4^{2-} \xrightarrow{k_{10}} i-C_8 + X^-$	kAB	5.63×10^{19}	4.10
$i-C_8 + X^- + i-C_4 \xrightarrow{k_6} i-C_8 + i-C_4 + X^-$	kAB	5.35×10^{10}	0.0
Destructive alkylation			
$i-C_7 + X^- \xrightarrow{k_{12}} i-C_7^{2-} + HX$	kA	7.49×10^5	1.08
$i-C_7^{2-} + i-C_4 + X^- \xrightarrow{k_{13}} i-C_5^{2-} + C_6 + X^-$	kAB	3.64×10^{21}	5.73
$i-C_5^{2-} + HX \xrightarrow{k_{14}} i-C_5 + X^-$	kAB	1.62×10^{11}	3.69
$i-C_5 + X^- + i-C_4 \xrightarrow{k_3} i-C_5 + i-C_4 + X^-$	kAB	3.29×10^{10}	0.0
$C_6 + X^- + i-C_4 \xrightarrow{k_4} i-C_6 + i-C_4 + X^-$	kAB	4.04×10^{10}	0.0
$i-C_7 + X^- + C_3^{2-} \xrightarrow{k_{15}} C_{10} + X^-$	kAB	3.72×10^{17}	2.59
$C_{10} + X^- + i-C_4 \xrightarrow{k_8} C_{10} + i-C_4 + X^-$	kAB	6.68×10^{10}	0.0
$i-C_5^{2-} + i-C_4 + X^- \xrightarrow{k_{16}} C_9 + X^-$	kAB	4.26×10^{19}	2.65
$C_9 + X^- + i-C_4 \xrightarrow{k_7} C_9 + i-C_4 + X^-$	kAB	6.02×10^{10}	0.0
$C_{10} + X^- \xrightarrow{k_{17}} i-C_5^{2-} + i-C_5 + X^-$	kA	4.45×10^{11}	8.40

^acm³/g·mole·s or s⁻¹.

^bkcal/g·mole.

conditions which improve alkylate quality. This is illustrated in Fig. 8. It is difficult to compare HF consumption with that for H₂SO₄ since sulfuric acid is generally regenerated off-site. HF dilution during alkylation is actually higher because of the higher reactor temperatures and higher hydrocarbon solubilities.

Temperature

Alkylate quality increases by about one octane number for each 11°C reduction in temperature. Sulfuric acid alkylation cannot be operated at high HF alkylation temperatures because of oxidation reactions.

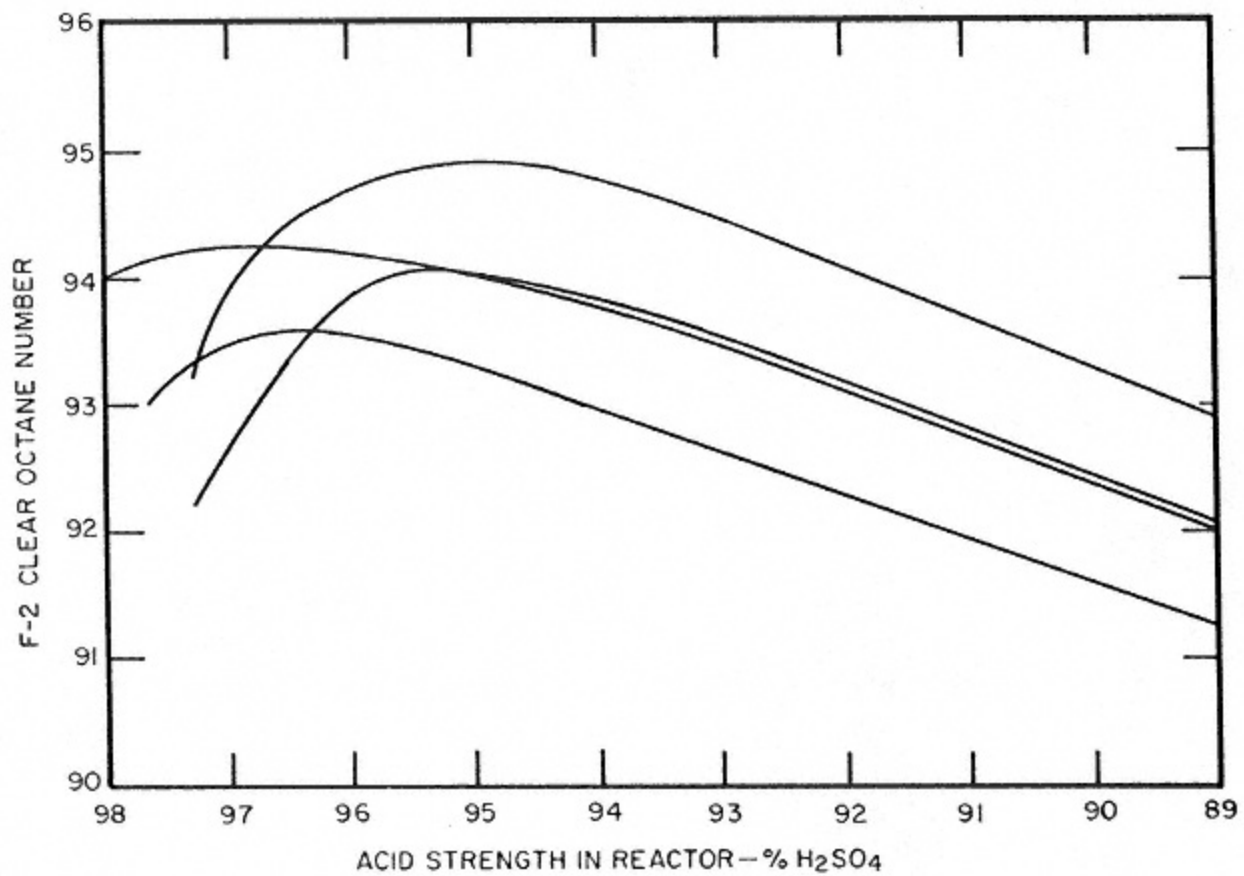


Fig. 7.

Effect of acid strength on octane number of total debutanized butene alkylate (different curves result from changing conditions other than acid strength) [128].

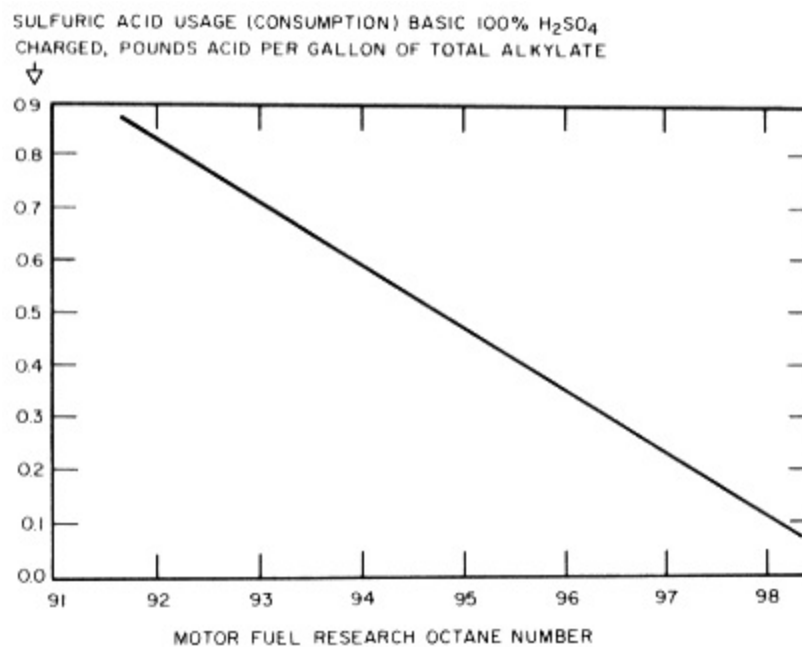


Fig. 8.

Relationship between alkylate quality and acid consumption for a typical butene feed [6].

Isobutane and Olefin Concentrations

A high isobutane to olefin ratio is necessary to maintain the concentration in acid necessary for primary alkylation and to suppress secondary reactions. This requires that isobutane be recovered from the reactor effluent stream. The quantity recovered and recycled is maintained as high as economically feasible. Alkylate quality increases nearly linearly with isobutane content in the hydrocarbon phase, Fig. 9. Commercially, the external ratios of isobutane to olefin in the feeds are kept in the range of 5:1 to 15:1 while the internal isobutane circulation to olefin feed ratio may be as high as 1000:1.

Concentration of olefins in the hydrocarbon is essentially zero since they are rapidly and nearly irreversibly absorbed in the acid phase. The olefin concentration in the acid must be kept low to minimize polymerization. Olefin effects are correlated to a space velocity factor as derived in the reaction section of this article (Fig. 10).

Olefin Feed Stock

The composition of olefin feed streams vary significantly with the local refinery situation. Nearby chemical plants often remove select olefins, for example, isobutene for secondary butyl alcohol, and return the unused olefins for the alkylation processes. These olefin streams also vary according to source, catalytic or thermal cracking, and unit conditions. Propene and pentenes are

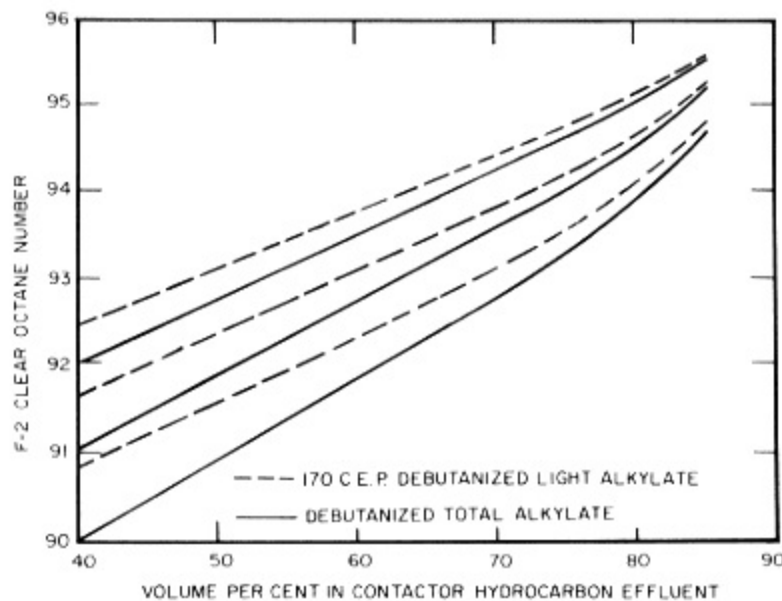


Fig. 9.
Effect of isobutane concentration on octane number of alkylate
(different curves result from changing conditions other than isobutane
concentration) [128].

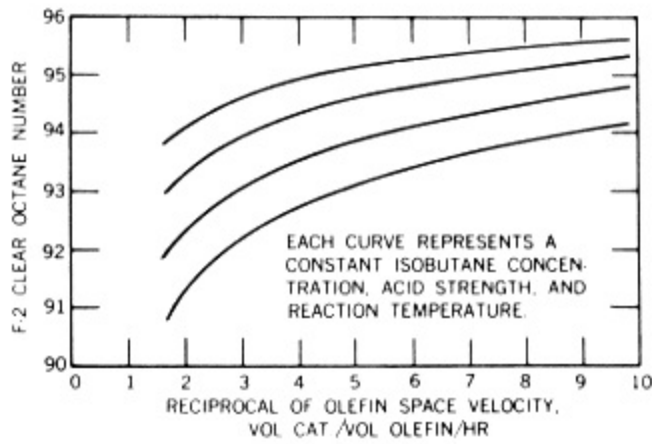


Fig. 10.
Effect of space velocity on octane number of butene total
alkylate [128].

also used as alkylation feeds under some conditions. Propene is more readily alkylated in the presence of butenes. However, both propene and pentenes produce lower quality alkylate and have higher acid consumption than butenes, Table 12.

Contaminants

Components other than isobutane and olefins in the hydrocarbon feed act either as diluents or deleterious reactants. Normal butane acts as a diluent and reduces the effective isobutane concentration. Its removal by distillation is an

TABLE 12 Typical Sulfuric Acid Alkylate Yield and Quality Data [7, 10, 75, 128, 140]

Olefin Feed	Propene	Butenes	Pentenenes
Isobutane consumed (vol/vol olefin)	1.271.32	1.101.16	0.961.14
Heat of reaction (Btu/lb olefin)	840	615	500
Total alkylate yield (vol/vol olefin)	1.751.78	1.701.72	1.551.60
Acid consumption lb acid (98% to 90%) per gal total alkylate	1.82.0	0.40.6	1.0
Antiknock properties			
F-1 clear	8992	9497	9293
F-1 + 3 cc TEL	101.6103	104.2106.2	103103.7
F-2 clear	8890	9294	91
F-2 + 3 cc TEL	99101	100104	98100
F-3 PN + 4.6 cc TEL	116	127132	122
F-4 PN + 4.6 cc TEL	135140	155160	145150

economic balance between n-butane content and loss of isobutane to the n-butane stream. Ethene forms stable esters with sulfuric acid and is a direct acid diluent. Butadiene is believed to be an acid diluent. Also, water, mercaptans, and hydrogen sulfide greatly increase acid consumption.

Performance Factors

In addition to the severity parameters developed earlier, a number of correlations have been published to predict alkylate yield and quality. They have the common characteristics that higher isobutane content and lower olefin space velocity increase alkylate yield and quality.

Emulsion characteristics and mass transfer limitations are important at the relatively low levels of mixing energies in commercial reactors (few tenths horsepower per barrel per day of total alkylate throughput). The effect of mixing energy was discussed previously. Best alkylates are obtained when the emulsions are "tight" acid continuous. However, at low acid contents the emulsions become inverted, or rather, contain large volumes of unemulsified hydrocarbon. The operational policy is usually to maintain as tight an emulsion as can be separated in the system settler.

Alkylation Plant Systems

Reactor designs have fairly well stabilized over the past decade. Emphasis has been on improving yield and quality of alkylate, reducing acid consumption, improving emulsion and reactor cooling control, and improving separation and control in the product recovery section, particularly for isobutane recycle.

Two reactor systems have prevailed for the H_2SO_4 process and two for the HF process. For sulfuric acid the Stratco horizontal contactor and the Kellogg cascade reactor are the principal systems. The first commercial reactor, the time-tank reactor, is losing favor. The two HF systems are the Universal Oil Products and Phillips reactors, both being tower-type contactors.

Time-Tank Reactor

The time-tank reaction system is a closed-loop circulation pipeline which includes a chiller, time-tank, and circulation (emulsifying) pump (Fig. 11). The time-tank contains a number of perforated or baffled plates to provide additional mixing of reactants as well as providing residence time. Circulation of the emulsion through the loop dilutes the olefin and provides good heat exchange in the tube-in-shell chiller. It also provides the turbulence for good contact between isobutane and acid. Circuit times are about 1 to 2 min while the average hydrocarbon residence in the loop (contact time) is 20 to 30 min. A continuous slip stream is routed to the settler, acid is returned to the loop, and hydrocarbon (settler overflow) is caustic and water washed before being routed to the distillation section.

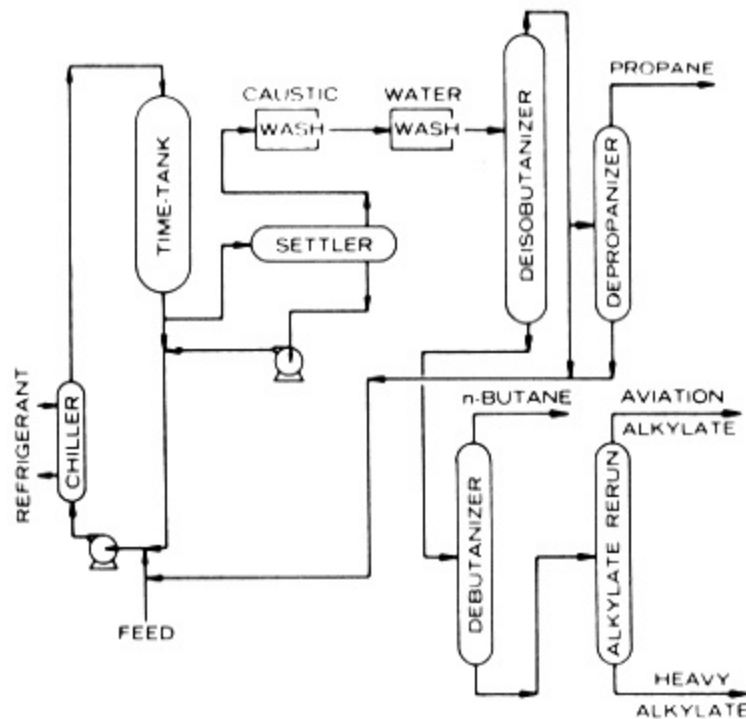


Fig. 11.

Isoparaffin/olefin alkylation process utilizing the time-tank reactor [26].

Horizontal Contactor

The contactor reactor is a well-mixed, draft tube vessel containing a heat-exchange tube bundle. The horizontal orientation provides considerable savings in construction and maintenance. The emulsion circulation path is around the outer shell and back through the exchanger tube bundle (Fig. 12). Circuit times are on the order of 10 s. Feed streams are introduced just upstream of the impeller, and a slip stream is withdrawn to the settler.

Effluent refrigeration is now the common practice (Fig. 13). Hydrocarbon from the settler, normally at 50 to 75 lb/in² gauge is throttled to 2 to 8 lb/in² gauge to partially vaporize the effluent. The resulting cool two-phase stream passes through the tubular heat exchange bundle. Vapors are recompressed, and after propane is removed they are returned to the reaction system.

Cascade Reactor

The cascade reactor is a compartmented, autorefrigerated series of reactor settlers (Fig. 14). Acid and recycle isobutane streams are introduced into the first compartment (Fig. 15). Cooling is effected by equilibrium vaporization at the system pressure, thus eliminating the need for a heat exchanger surface.

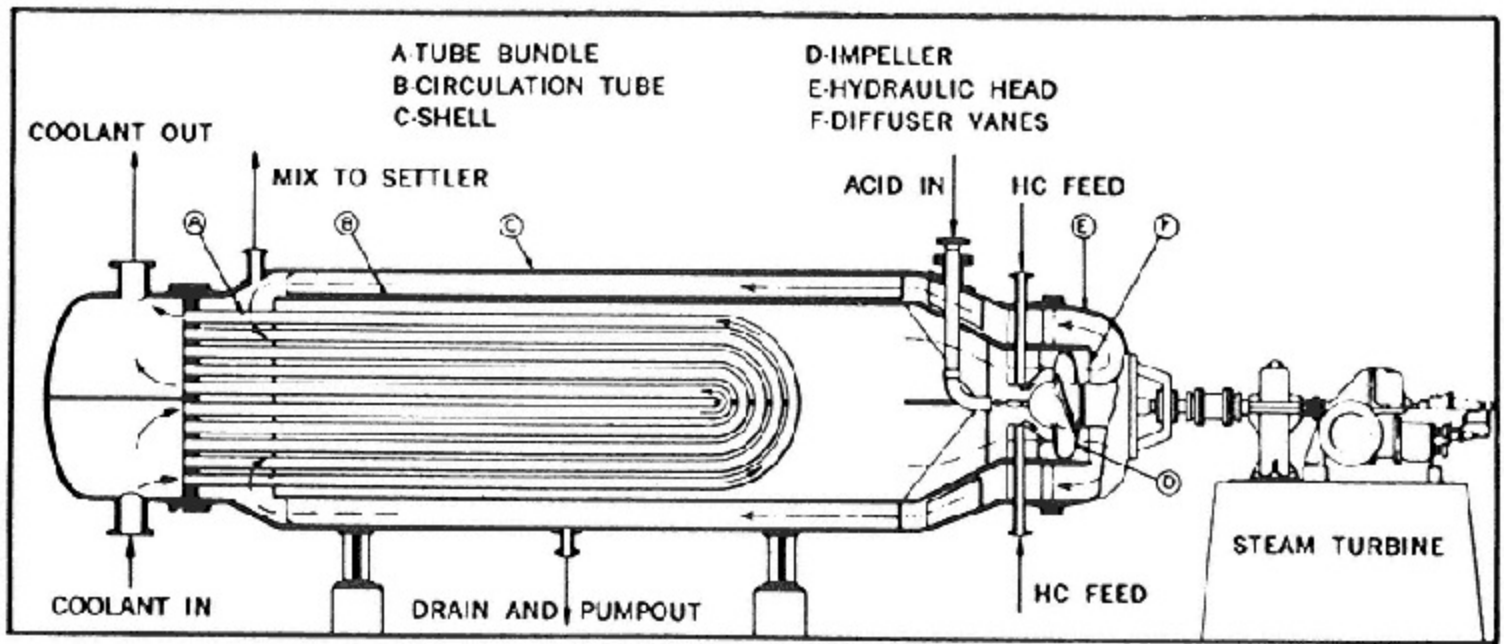


Fig. 12.
Details of the horizontal contactor
(sketch courtesy of Stratford Engineering Corporation).

Olefin feed is divided equally to each reaction compartment; a settler zone permits hydrocarbon and a small net flow of acid to overflow a weir into the next compartment. As in the effluent refrigeration system, the vapors are recompressed, condensed, and recycled to the reactor.

HF Reactor Systems

The simplified flow charts for the Universal Oil Products and the Phillips processes are similar (Figs. 16, 17, and 18). However, Phillips has integrated a

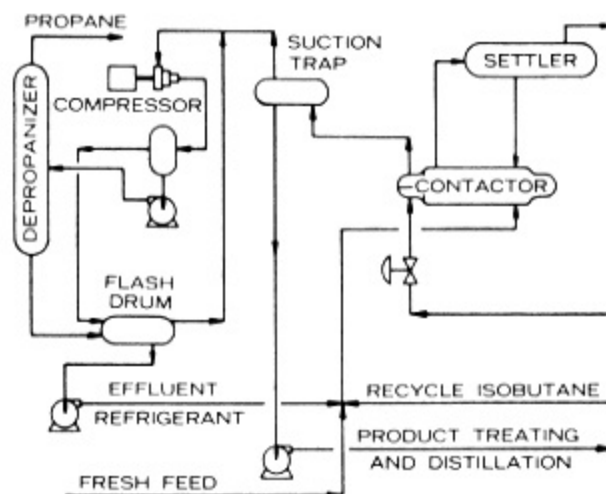


Fig. 13.
Contactor with effluent refrigeration [26].

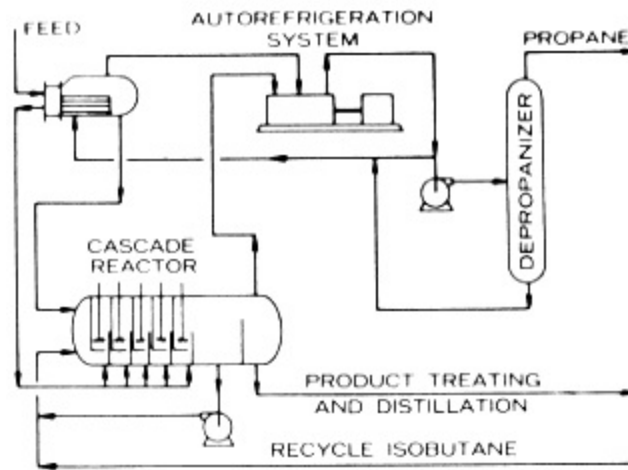


Fig. 14.
Cascade reactor with autorefrigeration [26].

propane disproportionation plant ("triolefin" process) and an ethene alkylation plant (AlCl_3 to produce diisopropyl as well as butene alkylates.

Feed driers are used to keep the water content of the HF below 2%. Feed is introduced into the bottom of a tower reactor through jets which provide sufficient agitation between hydrocarbon and catalyst. The recovery system is similar to H_2SO_4 except dissolved HF in hydrocarbon is also recovered by distillation.

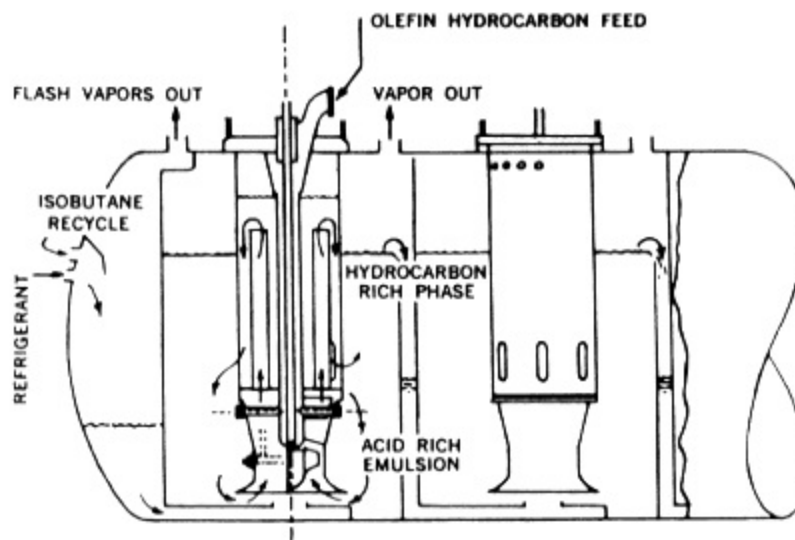


Fig. 15.
Cascade reactor
(sketch courtesy of the M. W. Kellogg Company).

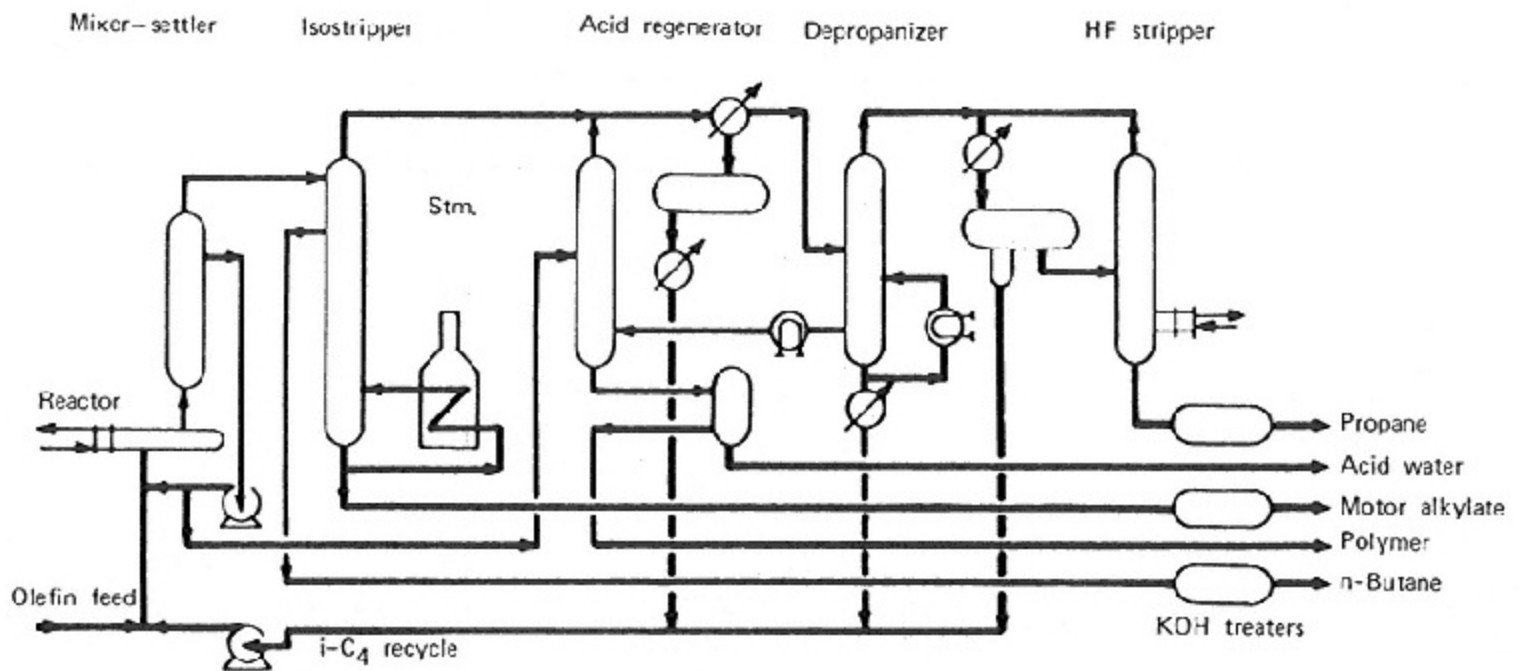


Fig. 16.
Union Oil Products hydrofluoric acid alkylation process
[R. C. Ewing, Oil Gas J., 69(33), 67(1971)].

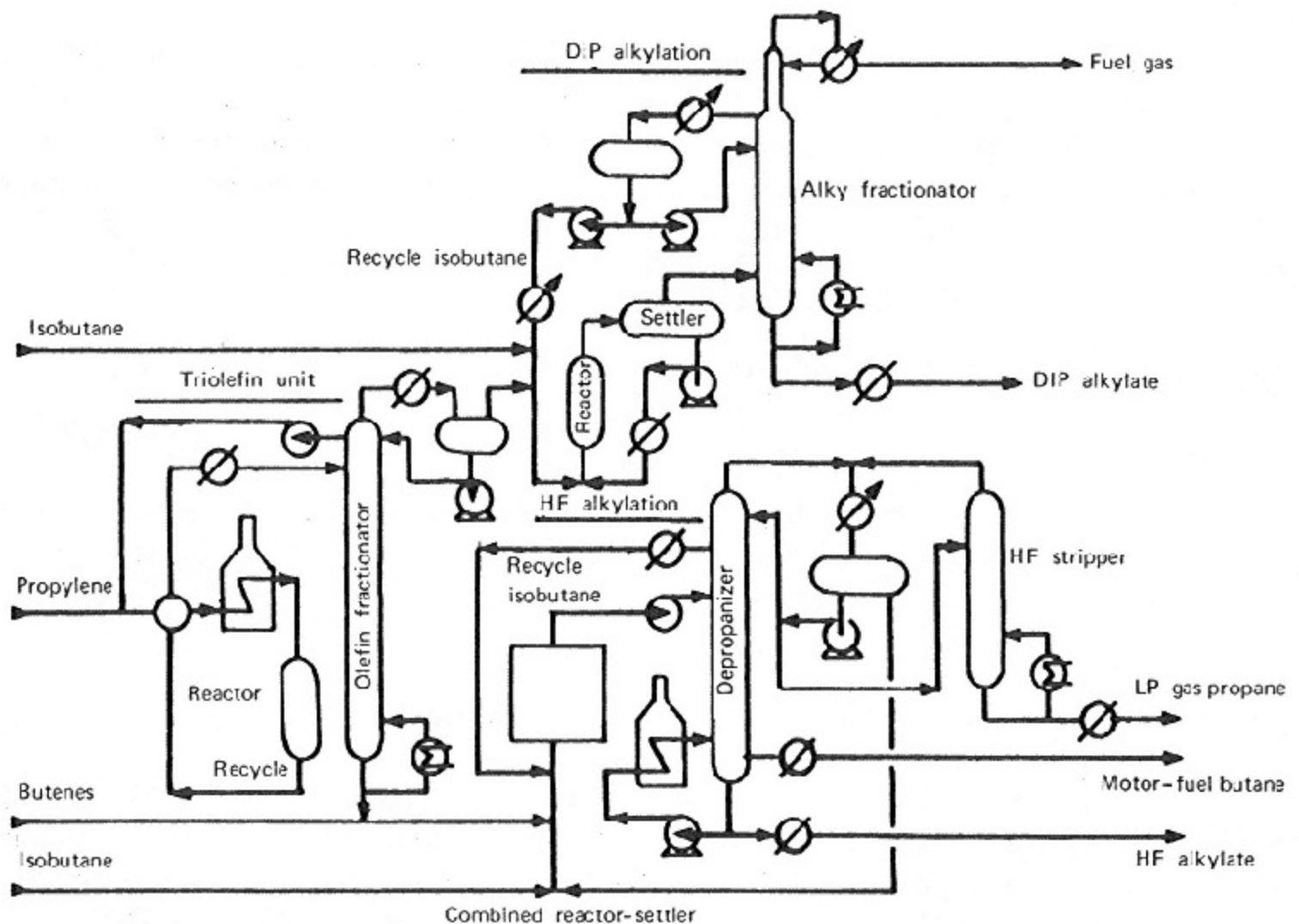


Fig. 17.

Phillip's hydrofluoric acid alkylation process
[R. C. Ewing, Oil Gas J., 69(3 70 (1971)).

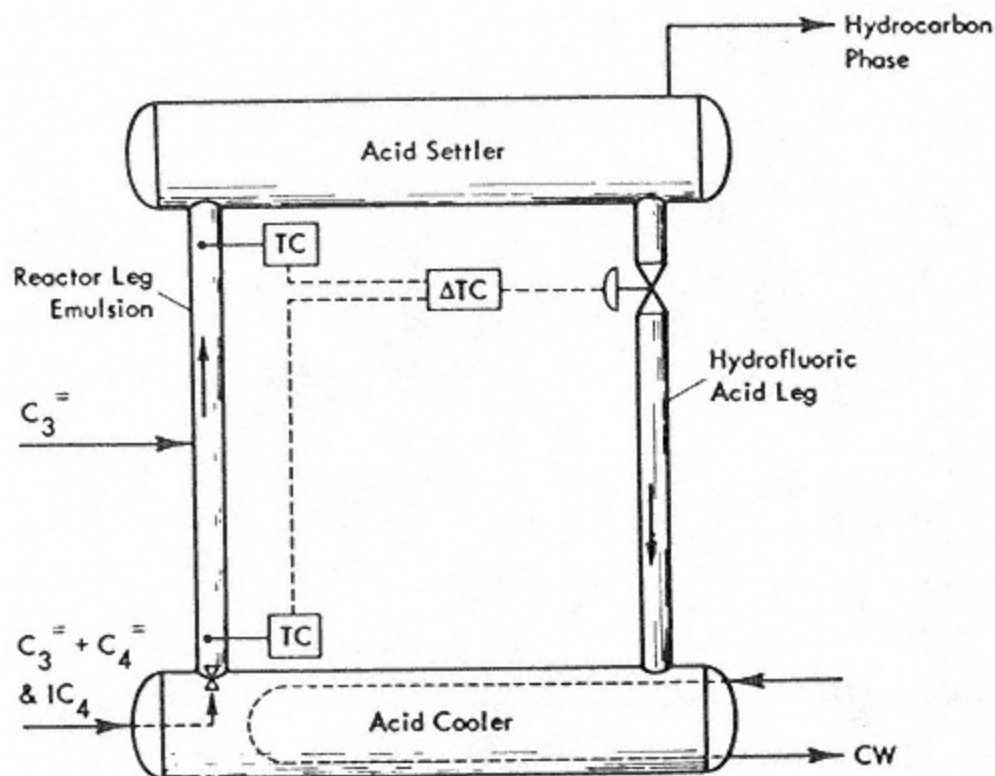


Fig. 18.
Phillip's reactor system [162].

Alkylation of Aromatic Compounds

The catalytic alkylation of aromatic hydrocarbons is a substitution reaction wherein one or more of the hydrogen atoms on the ring or on a side chain is replaced by an alkyl group. Both substituted and unsubstituted aromatic structures may be so alkylated. In general, the following overall reaction occurs:



These reactions can occur through electrophilic (acid-catalyzed), nucleophilic (base-catalyzed), or free radical mechanisms. The catalyst used dictates the mechanism by which the reaction occurs.

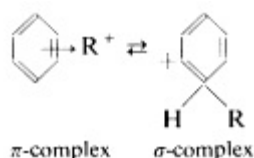
Electrophilic (Acid-Catalyzed) Substitution

Commercial alkylation of aromatic hydrocarbons is exclusively carried out via electrophilic substitution. The metal halides are the most commonly used catalysts. Burk [21] has listed the halides in order of decreasing activity: $\text{AlBr}_3 > \text{AlCl}_3 > \text{FeCl}_3 > \text{ZrCl}_5 > \text{TaCl}_5 > \text{BF}_3 > \text{UCl}_4 > \text{TiCl}_3 > \text{WCl}_6 > \text{ZnCl}_2 > \text{SnCl}_4 > \text{TiCl}_4 > \text{BeCl}_2 > \text{SbCl}_5 > \text{HgCl}_2 > \text{CuCl}_2 > \text{BiCl}_3 > \text{AsF}_3$. Aluminum chloride [66, 126] and boron trifluoride [150, 159] have been

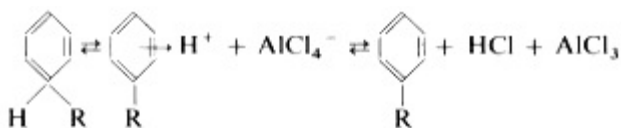
the most widely investigated and commercially used of these catalysts. Strong mineral acids such as HF [147], H₂SO₄ [49], and H₃PO₄ [72], used alone or supported on a substrate, have also been used as catalysts for this reaction. More recently, synthetic zeolites have been studied [81, 91, 106]. The mechanisms for all the reactions to be described are similar and in general follow the classic Friedel-Crafts path:



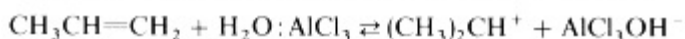
This reaction scheme is an overall path. In reality the catalyst initially forms a 1:1 addition compound with the alkyl halide [35]. The resulting carbonium ion then forms a so-called π -complex with the aromatic ring which ultimately transforms to a σ -complex:



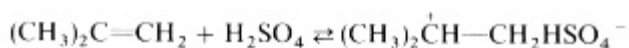
The proton now becomes π -complexed to the substituted ring before finally being released to reform the catalyst [107]:



In this mechanism an alkyl halide with aluminum chloride formed the intermediate carbonium ions which subsequently attacked the aromatic products sources of carbonium. These are alcohols, ethers, esters, and olefins. By far the most commonly used of these are the olefins. There is evidence that pure olefins do not react with pure metal halides [107]. HCl and water are used industrially to promote the formation of intermediate carbonium ions:

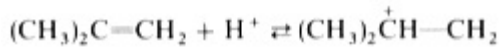


Strong acids such as HF, H₂SO₄, and H₃PO₄ [100, 107] also interact with olefins to form carbonium ions. Olefins containing tertiary carbon atoms such as isobutene form the more stable tertiary ions:



Recent experiments have demonstrated the viability of certain synthetic zeolites as catalysts for the alkylation reaction. The mechanism is essentially

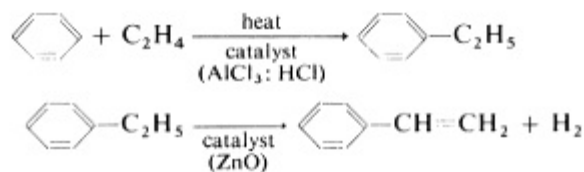
the same involving proton addition to the olefin at active acid sites on the surface of the zeolite:



Once the carbonium ions are formed, the reaction proceeds as shown above for the alkyl halide derived ions. This is not to say that all catalysts will perform equally well under the same conditions. In fact, for given olefins and/or aromatic compounds, certain of the catalysts are impractical because of detrimental side reactions. For example, ethene would require 98% H_2SO_4 for formation of secondary carbonium ions. Such strong acid would react with benzene to form some sulfonic acid; hence, for ethylation of benzene, AlCl_3 is a more selective catalyst. In the ensuing discussion the various commercially significant products formed via aromatic alkylation are discussed with emphasis on the particular catalysts best suited for the processes involved.

Ethylbenzene

Ethylbenzene is used almost exclusively for the manufacture of styrene via a catalytic process which selectively dehydrogenates the ethyl group. The reactions involved are as follows [100]:



Ethylbenzene is also used as a solvent and as an intermediate in dye manufacture. Approximately 10% of the ethylbenzene produced in the United States is a by-product of refinery operations. The remaining 90% is synthetically produced via alkylation of benzene with ethene [14].

A commonly used catalyst is aluminum chloride promoted by hydrogen chloride. HCl is formed by decomposition of ethyl chloride in the feed. Figure 19 shows a flow diagram of the liquid phase process [103].

As can be seen, the aluminum chloride is complexed with various reactor products ethyl chloride. These complexes have been the subject of considerable study [107, 159]. In general, their composition is as given by McAllister [100]:

AlCl_3	27%
Polyethylbenzenes	25%
Benzene and ethylbenzene	48%

Because the catalyst in this complexed state is virtually insoluble in the reaction products,

it may easily be separated from them. Fresh catalyst is very easily complexed in a simple mixing vessel. These factors, coupled with the high catalyst activity of the complexes, make them industrially attractive.

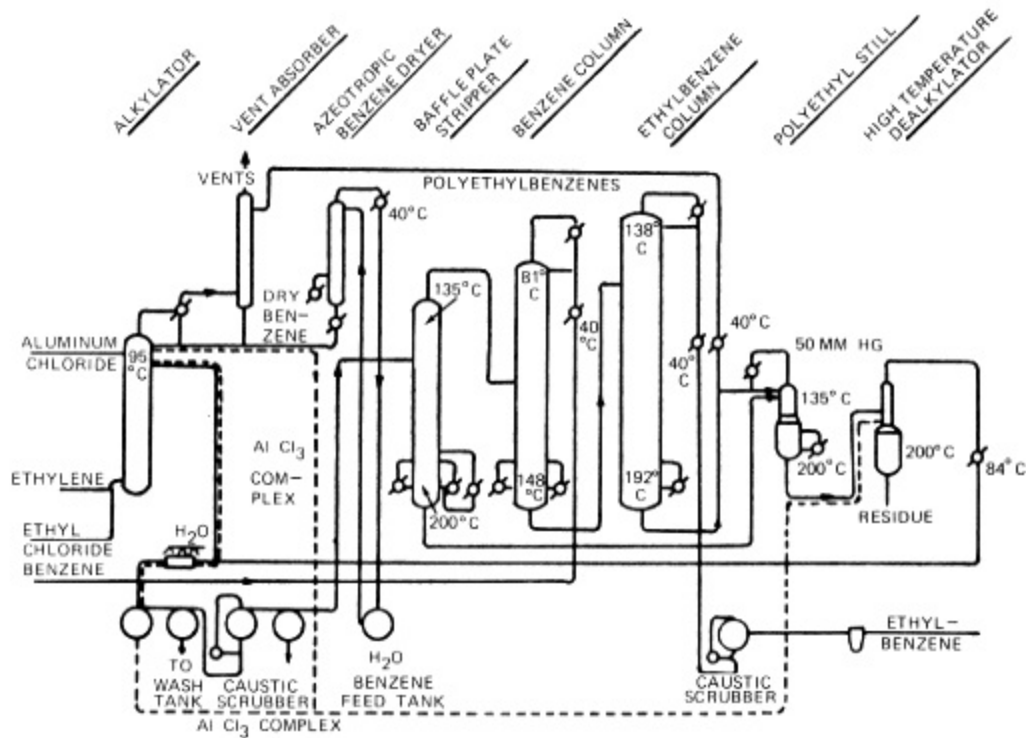


Fig. 19.

Liquid phase process for ethylbenzene production [103].

In the liquid phase process the reaction is carried out at pressures slightly above atmospheric and at about the boiling point of the reactants (80 to 100°C). The metal chlorides in the liquid phase, and in particular AlCl_3 , are highly corrosive. Therefore, the reaction vessels are ceramic or glass lined. Polyethylbenzene formation is minimized in commercial operation by increasing the benzene to ethene ratio [103]. At higher pressures the temperature of the reaction, and thus the reaction rate, can be increased without vaporizing the reactor contents. The benzene feed must be pure (around 99%) and the ethene feed must be 90% or better. Yields in the vicinity of 96% basis ethene and benzene are common. Catalyst consumption is in the range of 1 to 3 lb AlCl_3 /100 lb ethylbenzene [100, 133]. In the liquid phase process a step is included for dealkylating polyethylbenzenes to mono's and di's. Higher temperatures favor the dealkylation reaction. It is common practice, therefore, to effect this reaction in a separate vessel operated at higher temperature (200°C) in the vapor phase over an acidic supported type catalyst [100].

Ethene-benzene alkylation can also be carried out in the vapor phase over a different catalyst and under less corrosive conditions. In fact, most ethylbenzene is produced via the vapor phase reaction of ethene and benzene over phosphoric acid on kieselguhr, so-called solid phosphoric acid [73, 78, 99]. A flow diagram of the basic process is shown in Fig. 20 [77]. The selectivity of the reaction to

monoethylbenzenes is improved by operating at higher (5:1) benzene to ethene molar ratios. Higher pressures (up to 900 lb/in² gauge) and higher temperatures (to about 350°C) increase conversion. Catalyst decline which results from formation of carbonaceous material on its surface and loss of water is more severe at higher temperatures; hence it is preferable to operate at higher pressures and reduced temperatures [74]. To counteract dehydration, water is added to the feed. Catalyst life is about 350 lb ethylbenzene per lb of catalyst, but the catalyst can be regenerated by burning. The process can utilize feeds containing as low as 16% ethene; however, higher yields are obtained with higher purity feeds. The per pass conversion of ethene is approximately 50%. No dealkylator is required in this process.

A more recently developed process, called the Alkar process [54], utilizes a boron trifluoride catalyst supported on a modified anhydrous alumina [19, 42]. This catalyst will handle ethene feeds in the vicinity of 8 to 10%, and thus it can readily be adapted for use in the refinery. Temperatures in the vicinity of 300°C and pressures at 900 lb/in are preferred [55]. Polyethylbenzenes are dealkylated in a second reactor operated between 100 and 200°C and 500 to 550 lb/in. Yields are 95% and above basis ethene.

Many other metal halide, Friedel-Crafts type [104, 114, 123, 160] catalysts,

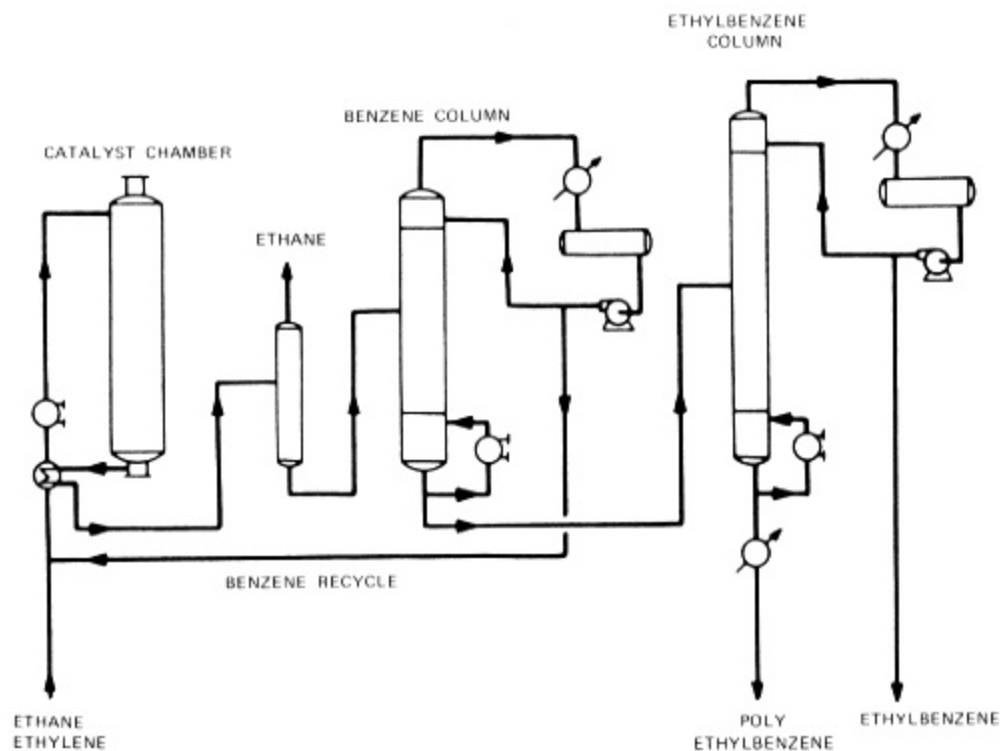


Fig. 20.
Vapor phase process for ethylbenzene production [77].

and mineral acid catalysts [116] have been tried in the laboratory. Excellent reviews of these attempts are given by Topchiev [158, 159].

Zeolitic-type catalysts have also been extensively studied for this reaction [89, 102]. Some of these processes have been commercialized; however, little, if anything, has been published on actual commercial experience. The amorphous aluminosilicates similar to those used in catalytic cracking have also been studied [113]. Such catalysts exhibit low per pass conversions, but polyalkylbenzene production is low and they can be recycled; also, these catalysts can easily be regenerated.

Cumene

Cumene (isopropylbenzene) processes were originally developed to meet the demand for aviation gasoline during World War II. With the advent of the jet age, cumene is no longer synthesized as a pure compound to be used as a high octane blending component in motor fuels. Cumene for this purpose is produced as a by-product in refinery operations. Today approximately 65% of the cumene manufactured as a pure compound is used in making phenol, with 34% ending up as by-product acetone. The remainder is used in the manufacture of α -methylstyrene [9, 13].

Cumene is manufactured commercially in a vapor phase process using the solid phosphoric acid catalyst developed by Universal Oil Products [73]. A simplified flow diagram is shown in Fig. 21.

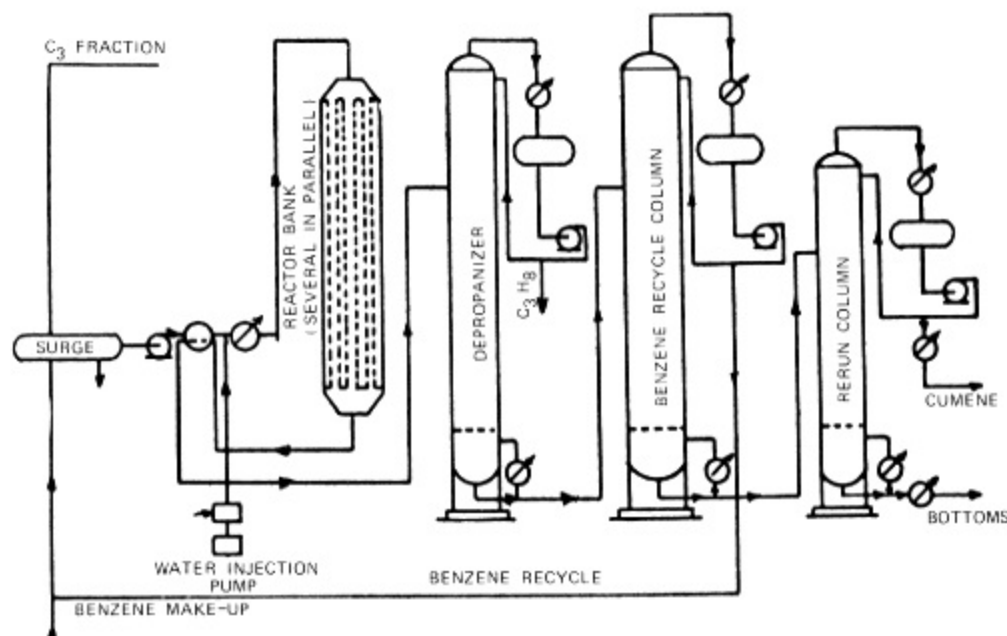


Fig. 21.
Flow diagram for vapor-phase cumene production [101].

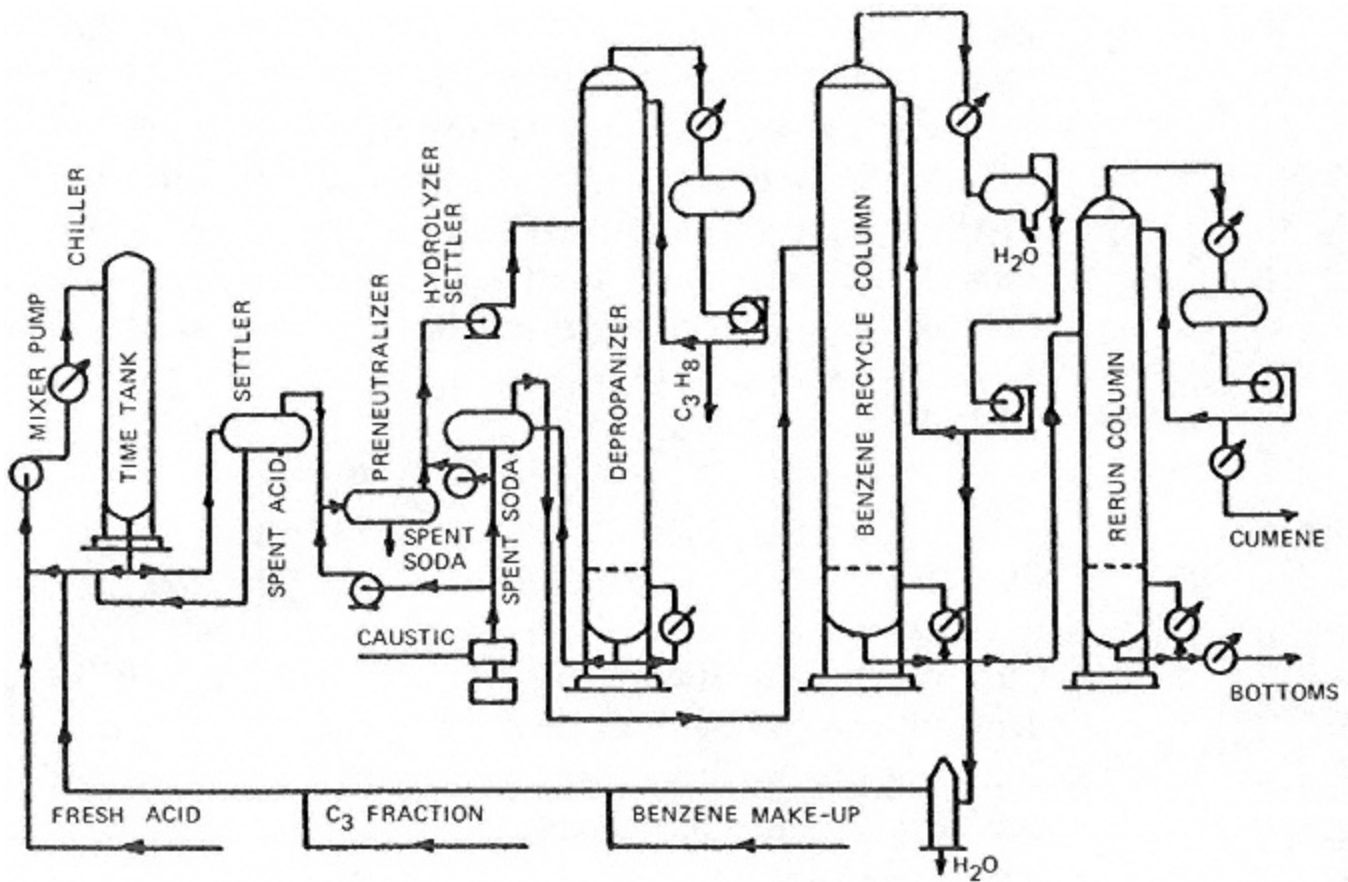


Fig. 22.

Flow diagram for liquid-phase cumene production [101].

The thiophene content of the benzene feed must be kept below 0.15% to maintain reasonable catalyst lives. H_2SO_4 washing of the benzene feed will selectively remove thiophene. The propylene feed is caustic washed to remove mercaptans which also adversely affect catalyst life. Purified benzene and propene feeds are fed in a mole ratio of at least 5 to 1 to the reactor in order to achieve about 94% conversion of the propene. Lower mole ratios lead rapidly to lower conversions (e.g., 4 to 1; conversion is 70%). Higher mole ratios do not significantly improve conversion above 94%. The reaction is conducted at 200 to 500 lb/in² and 200 to 250°C. Increasing temperatures and pressures in these ranges increases conversion but not yield. Approximately 1.70 vol of cumene are produced per vol of propene, and catalyst life ranges from 100 to 200 gal cumene/lb catalyst.

Cumene can also be produced via liquid phase process. The catalyst most often used in this type of plant is sulfuric acid. A simplified flow diagram of this process is shown in Fig. 22 [101]. The process is somewhat more complicated, and corrosion is a more severe problem than in the vapor phase process. Stratcos or time-tank reactors, as discussed earlier in isoparaffin-olefin alkylation, can be used in essentially the same configurations to create circulating emulsions of sulfuric acid and reacting hydrocarbon into which the benzene and propylene feeds are injected. Fresh acid strengths must be below 90% to avoid direct sulfonation of the benzene ring. Temperatures range in the vicinity of 35 to 40°C and pressures are about 165 lb/in². A total of 99% of the propene is converted at

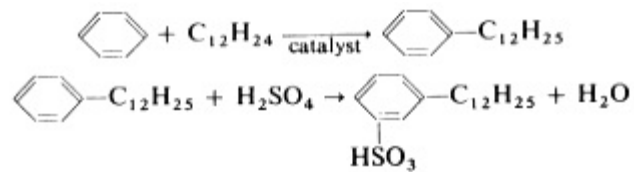
molar ratios of 6 to 1 benzene to propene. Acid life ranges from 10 to 12 vol of cumene produced per vol of fresh acid [100].

The two processes described above are the only commercially significant

processes for cumene in the United States. Of these the vapor phase process is the most widely used [158]. Benzene-propene alkylation has been studied extensively by Nieuwland [150] and Topchiev [158] in the presence of promoted and unpromoted metal halide type catalysts (particularly BF_3) to find the optimal catalyst for the reaction and to gain a better understanding of the mechanisms involved. Zeolites have also been tried for this reaction. None of these latter processes have been commercialized in the United States.

Dodecylbenzene

Aluminum chloride, hydrogen fluoride, and sulfuric acids are all widely used as catalysts for the alkylation of dodecene and benzene to form dodecylbenzene (detergent alkylate) which is then sulfonated to form dodecylbenzenesulfonates which are widely used in many commercial detergent products. The reactions involved are:



Olefin for this reaction is preferably propene tetramer obtained by polymerization of refinery C3 fractions over solid phosphoric acid catalyst in the vapor phase at 150 to 250°C and 200 to 600 lb/in². The resulting polymer, boiling in the 170 to 270°C range and containing 60 to 80% propene tetramer and 40 to 20% pentamer, is the preferred feed for the alkylation step. Highly branched alkyl groups are not desired; hence polymer derived from butenes does not

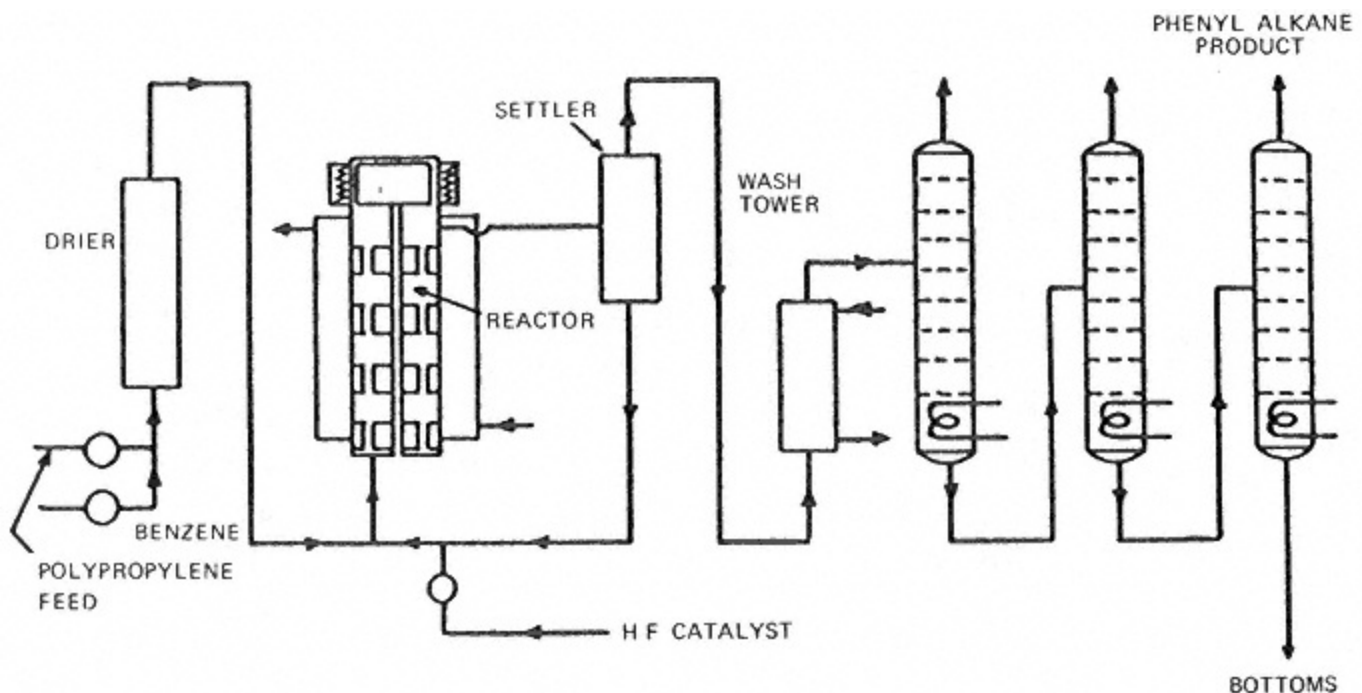


Fig. 23.
Process for manufacture of aryl-substituted alkanes [93].

make good detergent alkylate. For dodecylbenzene, three to five methyl groups on the alkyl side chain are ideal [100].

A simplified flow diagram of an HF process [93] for manufacture of detergent alkylate is given in Fig. 23. The exothermic reaction is conducted at 10°C and atmospheric pressure; hence refrigeration is required. Acid strength is maintained at 79% HF. This requires 0.26 vol of 100% HF per vol of polymer feed. High, 10:1, benzene to polymer ratios are required to produce essentially stoichiometric yields of alkylate. Sulfuric acid processes also operate best at about 10°C. About 1.15 lb of acid make-up per pound of alkylate is required to maintain acid strength in the reactor close to 100% H₂SO₄. Low, 3.5:1, benzene to polymer mole ratios are utilized in the sulfuric acid process.

Detergent properties are not only dependent on the degree of branching of the alkyl group but also on the position of the phenyl group on the dodecyl chain [17, 52]. Initially its position is mainly dependent on the position of the double bond in the dodecene molecule; however, isomerization occurs and in general all possible phenylalkane isomers are obtained in equilibrium mixture. This is observed for aluminum chloride catalysts; however, sulfuric acid and hydrofluoric acids do not achieve equilibrium mixtures, indicating that isomerization does not proceed as readily with these catalysts [115]. In the case of sulfuric acid and hydrofluoric acid [3], the amount of catalyst and the presence of inert diluents can also affect the product distribution.

Substituted Benzenes

The alkylation of benzene with various olefins rarely selectively produces only the monoalkylated benzene compound. Rather, mixtures of di, tri, and higher substituted structures are also formed. In fact, once one alkyl group has been added, its nucleophilic nature tends to make the resulting aromatic structure even more reactive by increasing the availability of π -electrons. The directing effect of alkyl substituent groups is steric rather than polar in alkylated benzene structures. Thus, in nitration of monoalkylbenzenes, if the substituent group is a methyl group as in toluene, the substitution will occur primarily in the ortho and para positions, whereas if the substituent group is a tertiary butyl group, much less ortho substitution will occur with a corresponding increase in substitution at the meta and para sites [107].

The steric complexity of the substituting group also has a directing effect. For example, in the monoalkylation of toluene, if the entering group is methyl, mainly ortho and para substitution occurs. A tertiary butyl group, on the other hand, will almost exclusively enter in the para position. These directing effects have been used in a variety of applications to produce in the laboratory just about any conceivable substituted benzene structure and isomers thereof. Commercially, polyalkylbenzenes are the chief by-products of cumene and ethylbenzene manufacture. Alternatively, sulfuric and phosphoric acid as well as aluminum chloride and boron trifluoride have all been successfully used as catalysts for the direct synthesis of these products, depending on the particular polyalkylbenzene

desired [2, 86, 134, 165].

The dialkylated benzene structures are of most importance industrially. Diisopropylbenzene, for example, can be converted by air oxidation to terephthalic acid, an important intermediate in synthetic fiber manufacture. Another oxidation product of diisopropylbenzene, isophthalic acid, is an important base material for alkyd resins [49]. Dialkylbenzene can be dehydrogenated to divinylbenzenes which are intermediates in the manufacture of ion-exchange resins. Tri and higher alkylbenzenes can be used as rubber and elastomer extenders [31].

Polycyclic Hydrocarbons

Alkylsubstituted polycyclic aromatic compounds are used as synthetic lube oils or as pour point depressants in other lube oils. Derivatives of such compounds have been used as emulsifying agents and detergents.

Naphthalene can be alkylated with ethene at 250°C over P_2O_5 [97] to form ethyl- and diethylnaphthalene. Orthophosphoric acid at 200°C will alkylate naphthalene and propene to form isopropylnaphthalene [69], while with HF at 0 to 20°C tetraisopropylnaphthalene is formed [22]. Aluminum chloride also catalyzes the reaction of olefins with naphthalene [4] to form mono- and polyalkylnaphthalenes.

In general the alkylation of naphthalene with olefin, regardless of the catalyst, yields a variety of products. Rarely is the reaction purely selective to the monoalkylnaphthalene. Topchiev [159] has reported, however, that $BF_3 \cdot nH_2O$, $BF_3 \cdot H_3PO_4$, and $BF_3 \cdot HF$ catalysts have been used successfully to synthesize monoalkylnaphthalenes selectively from naphthalenes and olefins. Beginning with propene, the yield of alkylate in such reactions decreases with increasing carbon number of the olefin but increases with temperature and residence time. $BF_3 \cdot H_2SO_4$ catalysts do not alkylate due to reaction of the sulfuric acid with the naphthalene directly to form sulfonic acids.

Dealkylation/Transalkylation

Many of the catalysts used to alkylate aromatic compounds can be used at elevated temperatures to reverse the alkylation reaction. This is particularly important in some processes where significant quantities of polyalkylbenzenes or naphthalenes are formed. In general, these processes are conducted in the vapor phase and many of them in the presence of H_2 .

Universal Oil Products' Hydeal process is used commercially to dealkylate toluene or methylnaphthalene to benzene and naphthalene [20, 38] in the presence of H_2 .

The Tatorary process [8] uses a proprietary catalyst to form benzene and xylenes from toluene and trimethylbenzenes. Operating conditions range from 150 to 750 lb/in² and 350 to 530°C. H_2 consumption is claimed to be less than 9 lb/1000 lb of fresh toluene. Other catalysts for dealkylation/transalkylation

include Group VIII metal containing crystalline alumina-silicates [122] and AlCl_3 [82]. Aluminum complexes of carboxylic acids have been found useful in dealkylating substituted phenols [32].

Thermal hydrodealkylation at temperatures of 700°C and with molar hydrogen to oil ratios of at least 2 is also practiced commercially [46, 129]. Finally, steam dealkylation of alkylbenzenes has been demonstrated at temperatures in the range between 380 and 600°C over catalysts consisting of Group VIII metals over aluminas and aluminosilicates [98, 129]. The advantage of steam dealkylation is, of course, the lower cost of making steam as opposed to a relatively pure hydrogen stream.

Free-Radical Substitutions

Free radicals are electron-seeking species. With a preponderance of π -electrons in the aromatic ring it should be possible to couple free radicals to aromatic ring structures. A convenient source of free radicals is the greatest problem encountered in free-radical alkylation. Phenyl radicals are easily generated by thermal decomposition of benzoyl peroxides, and subsequent alkylation of benzene and substituted benzenes occurs readily. Methyl radicals can be generated by thermal decomposition of lead tetraacetate [44]. The methyl free-radicals are much less active than phenyl radicals in hydrogen abstraction or substitution into aromatic rings; even so, yields in the order of 18% of a toluene derivative (benzyl acetate) have been observed. Free-radical processes for aromatic alkylation have not been commercialized as yet; however, patents describing various processes have been issued [139].

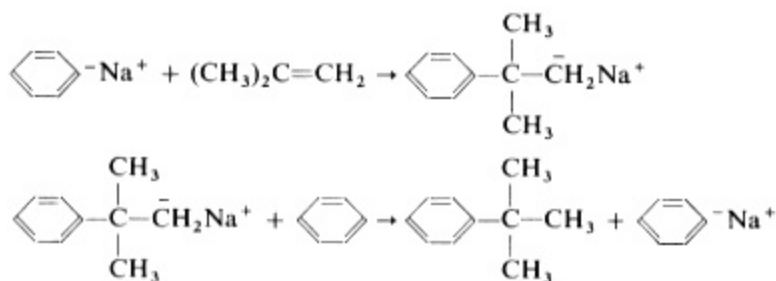
Nucleophilic (Base-Catalyzed) Substitutions

One of the possible fragments which can result from breaking of the R:H bond in a hydrocarbon is a carbanion:

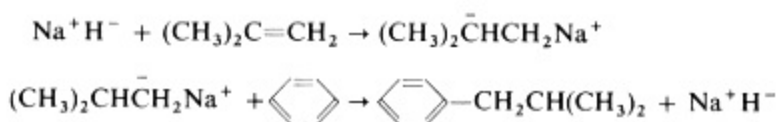


It is left with both electrons and thus carries a negative charge.

Benzene alkylation with olefins can be catalyzed through such intermediate carbanions by lithium, sodium, or potassium, their hydrides, benzylna, or reaction products of sodium with promoters such as o-chlorotoluene or anthracene [120]. Only small yields of alkylate are observed with sodium at 300°C [119]. Potassium-catalyzed reactions at 194°C give somewhat larger yields [118]. With both catalysts, however, the alkylation is accompanied by the formation of biphenyls. In view of this poor selectivity and yield, it is not surprising that the relatively facile acid-catalyzed alkylation of benzene has found much wider commercial application. Two mechanisms for base-catalyzed benzene alkylation are shown below, one for the benzylna catalyst and the other for sodium hydride which results from biphenyl formation:



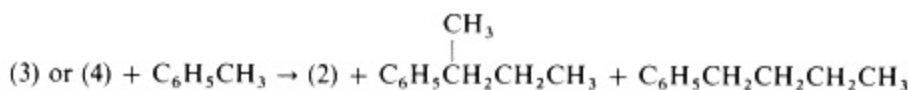
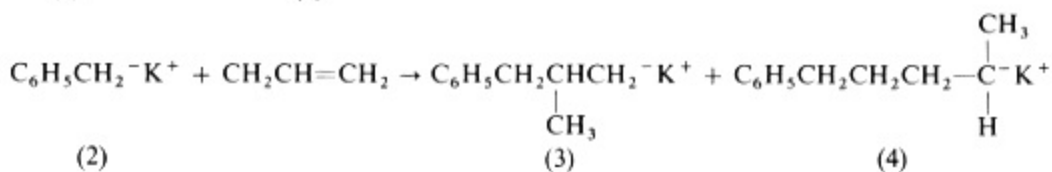
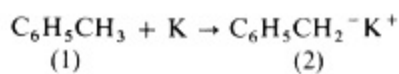
Benzyl sodium



Sodium hydride

Both products, namely tert-butylbenzene and isobutylbenzene, are observed as products when benzene is reacted with isobutene at 300°C [119] in the presence of the sodium catalyst.

Ring alkylation does not occur in base-catalyzed alkylations so long as benzylic hydrogens (hydrogens on the α -carbon) are available. This is in contrast to acid-catalyzed alkylations in which the ring hydrogens are always substituted. The utility of such reactions is that it allows the alkyl groups of alkylbenzene compounds to be enlarged. Thus toluene and propene can be alkylated at 149°C in the presence of potassium catalyst to yield 75% butylbenzenes as a mole percent of propene reacting [141] according to the following mechanism:



Both isobutylbenzene and n-butylbenzene are formed, however, in the ratio of 10 to 1, respectively. This points out, in contrast to the relative stability of carbonium ions, that the stability of carbonions decreases in the order: primary > secondary > tertiary.

Olefins which can be reacted include ethene, propene, and, to a lesser extent, butene. Reaction temperatures range between 150 and 300°C, increasing with increasing carbon number of the olefin. Catalyst activity increases in the order: lithium < sodium < potassium. Other reagents include diolefins such as

TABLE 13a United States Production of Four Major Alkylates^b

Product	Reactants	Catalyst	Temperature (°C)	Pressure (lb/in ²)
Isoparaffin alkylate	Olefin (propene, butenes) and isobutane	H ₂ SO ₄	010	135
		HF	040	135
Ethylbenzene	Ethene and benzene	AlCl ₃ -HCl	93	15
		Supported H ₃ PO ₄	200250	500900
		Alkar	150250	400700
Cumene	Propene and benzene	H ₂ SO ₄	3540	165
		Supported H ₃ PO ₄	180	500
Dodecylbenzene (detergent alkylate)	Propene trimer and benzene	HF	10	
		AlCl ₃ -HCl	5560	
		H ₂ SO ₄	1020	

^aThis table is an updated reproduction of Table 1 in Ref. 133.

^bU.S. Tariff Commission Report, Synthetic Organic Chemicals, U.S. Production and Sales, 1970 TC Publication 34.

^cMolar ratio of isobutane or benzene to olefin.

(table continued on next page)

(table continued from previous page)

Product	Contact Time (min)	Molar Ratio	Catalyst Consumption	Trans-alkylation	Production
Isoparaffin alkylate	540	814	0.32.0 lb/gal alkylate		529,180 bbl/d
	525	814	0.20.8 lb/bbl alkylate		310,900 bbl/d
Ethylbenzene	2.0 510	13 lb/100 lb ethylbenzene 50 gal ethylbenzene/lb catalyst		Yes	4837 × 10 ⁶ lb/yr
				No	
				Yes	
Cumene	35	6 10	1012 vol cumene/vol H ₂ SO ₄ 200 gal cumene/lb catalyst	No	1983 × 10 ⁶ lb/yr
				No	
Dodecylbenzene (detergent alkylate)	8 60	13 lb AlCl ₃ /150 lb alkylate 0.87 lb alkylate/lb H ₂ SO ₄		No	553 × 10 ⁶ lb/yr
				No	
				No	

butadiene and isoprene which react at 50 to 94°C in the presence of a sodium catalyst to form phenylalkanes [61, 166]. Styrene reacts at 80 to 125°C in the presence of a promoted sodium catalyst to form diphenylalkanes [121].

Alkylate Production

Table 13 presents the production of four major alkylates produced in the United States. The figures for isoparaffin alkylates are as of January 1, 1974. Since 1960 the production of sulfuric acid alkylate has increased by about 80%. HF alkylate production has more than tripled in this time. The reason for this has been the abundant supply of light olefins and isobutane spurred on by tremendous increases in the demand for gasoline.

The production values for the other three alkylates listed are for 1970. Ethylbenzene production tripled between 1960 and 1970. Virtually all of the ethylbenzene manufactured in the United States goes into the production of styrene which is a major component in the synthetic rubber used to manufacture automobile tires.

Cumene production has increased eightfold in the sixties, reflecting an increase in the demand for phenol which is ultimately used in the manufacture of phenolic resins and caprolactam, an intermediate in nylon-6 fibers manufacture.

Detergent alkylate manufacture increased by only 12% in the sixties, undoubtedly reflecting the development and marketing of more efficient detergents.

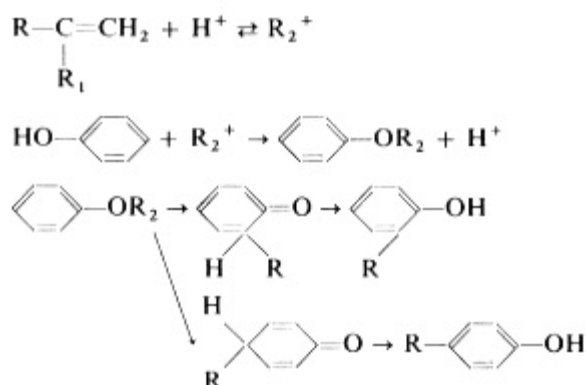
Alkylation of Oxygen Compounds

The alkylation of oxygen-containing compounds includes those of phenol with olefin to form alkylphenols, organic acids with olefins to form esters, and finally of alcohols and phenols with olefins to yield esters. All these products are extremely valuable as intermediates in other chemical processes or as final products in themselves.

Alkylphenols

The nucleophilic nature of the hydroxyl group in phenol increases the availability of π -electrons on the aromatic ring. Hence electrophilic substitution of hydrogens on the ring occurs at milder conditions than required for aromatic hydrocarbons. Catalysts which form intermediate carbonium ions from the olefin are used to effect substitution primarily in the ortho and para positions. For the lower molecular weight olefins through octenes, effective catalysts are sulfuric acid [155], orthophosphoric acid [71], hydrofluoric acid [148], and boron trifluoride [158, 159]. The reaction proceeds through Markov-

nikov addition of the phenol to the olefin to form an alkyl phenyl ether which isomerizes to ortho or para quinoid structures and finally into more stable alkyl phenols according to the following mechanism:



The relative amount of ortho and para substitution is a function of the catalyst, the amount present, and the reaction temperature [154]. Formation of alkyl aryl ethers can be significant at low temperatures with small amounts of catalyst. At higher temperatures and increased acid strengths and amounts of catalyst, alkylphenols are produced in greater yields. Propene [151], isobutene [88], and branched pentenes [84] are all used as feeds for preparing o- and p-tert-alkylphenols at temperatures ranging between 50 and 350°C. The various alkylphenols are useful as oxidation inhibitors in lube oils and as detergents, bactericides, fungicides, and disinfectants [47, 125].

Solid or fixed-bed catalysts are used to avoid the sometimes difficult separation of catalyst and reaction products in homogenous catalytic systems. Aluminosilicates catalyze phenol/isobutene alkylation to give primarily ortho derivatives at 120 to 150°C [112].

Alternatively, para substitution predominates at 80 to 120°C with cationic exchange resins of the sulfonic acid type such as Amberlite IR-112, Power 50-X12, and Permutite Q [95]. Methanol will alkylate with phenol to form cresols substantially free of meta isomers at 215 to 230°C in the presence of methyl or ethyl sulfonic acid catalysts [80]. Further alkylation of cresols with isobutene can be conducted in the presence of 5% by weight of 96 to 98% sulfuric acid or 104% fuming sulfuric acid to form tertiary butyl and dibutylmethylphenols. The amount of catalyst is critical in that less than 3% lowers yield significantly while more than 5% leads to isobutene polymerization [164]. It is also found that alkylation of tertiary olefins with p-cresol in the presence of BF_3 yields the expected ortho substitution to form tert-alkylmethylphenols only when the amount of catalyst relative to reactants is low (1 to 25 mol%). At higher concentrations (50 mol%), sec-alkyl phenols and saturated hydrocarbons are formed [96].

Alkylation of 2-butene with phenol in the presence of BF_3 yields a complex mixture of alkylated secondary butyl-, octyl-, and dodecylphenols which are useful as intermediates in the manufacture of biodegradable surface-active agents [111]. Propene and isobutene polymers can be alkylated by sulfonic acid resins at 70 to 100°C [95] to also yield octyl-, nonyl-, and dodecylphenols.

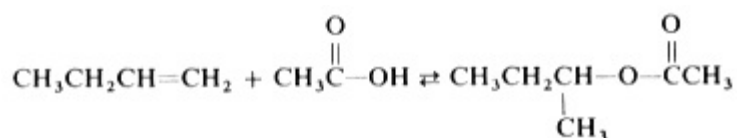
Other catalysts and respective reaction temperatures include Superfiltrol Clay at 80°C [45] and p-toluenesulfonic acid (p-CH₃C₆H₄SO₃H) at 80 to 150°C [1]. High molecular weight (C₁₄₂₀) α -olefins can be alkylated with phenol in the presence of an aluminosilicate catalyst. Reaction temperatures range between 100 and 276°C at 1 to 5 atm. The yield of alkyl phenols increases with temperature, residence time, and catalyst concentration [124].

Metal-catalyzed alkylation of phenols leads almost exclusively to orthosubstituted alkylphenols. Phenol, cresols, and naphthols can all be alkylated. Metals such as magnesium, aluminum, and zinc which form metal salts of phenol are effective catalysts. Kolka et al. [88] have studied the reactions of phenol with olefins in the presence of aluminum phenoxide Al(OPh)₃-type catalysts. Reaction temperatures ranged between 65 and 320°C. The various olefins tried included ethene, propene, and isobutene. In line with carbonium ion mechanisms, the reactivity of the olefins decreased in the order: isobutene > propene > ethene. Reaction conditions were found (105 to 115°C, 30 to 100 atm) whereby significant yields of mono- and di-tert-alkylphenols could be obtained concurrently. Previous attempts at this have necessitated a two-step process [57]. A similar product distribution is obtained when Cl₂ is added to the reactants and Al(OPh)₃ catalysts [27].

Esters

The alkylation of organic acids with olefins leads to formation of esters which are useful as plasticizers, solvents, and as chemical intermediates [48]. The direct esterification of olefins with organic acids possesses distinct advantages from a processing standpoint over the two-step process of olefin dehydration to an alcohol and subsequent esterification of the alcohol with an organic acid [105]. Catalyst inefficiency, resulting in lower yields, has, however, restricted the extensive use of the direct alkylation process on a commercial scale. One exception to this is the alkylation of α -pinene with carboxylic acid to form bornyl esters which are important intermediates in the camphor synthesis [85].

Secondary esters are commercially more desirable than the more readily hydrolyzed tertiary esters, hence secondary olefins are the primary starting materials for the reaction [41]. The alkylation proceeds through Markovnikov addition of the organic acid to the olefin. For example, in forming sec-butyl acetate the reaction is:



Olefins which can be alkylated range from ethene to octenes and higher and cyclohexene. Carboxylic acids which can be reacted include mono- and dibasic aliphatic, aromatic, and phenolic acids, and halogen-substituted acetic acids [158].

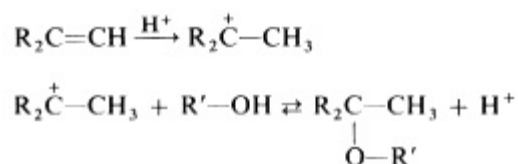
The reactivity of the carboxylic acid in adding to olefins decreases as the size

of the hydrocarbon group attached to the carboxyl group increases. Hence formic and acetic acids are more reactive than propionic and butyric acids. The dibasic acids are more difficult to alkylate, while aromatic acids and halogensubstituted acids are highly reactive.

Catalysts which are used for this process include sulfuric acid [41], boron trifluoride [30, 152], boron trifluoride etherate [158], and boron trifluoride-hydrogen fluoride [105]. Reaction temperatures range between 20 and 150°C depending on the reagents and the catalyst. Higher temperatures in general lead to higher reaction rates and higher yields of esters. However, dissociation of the ester and polymerization of the olefin can occur at higher temperatures. For most reagents and catalysts, therefore, an optimum reaction temperature exists. Thus the reaction of acetic acid with 2-butene in the presence of BF₃ etherate leads to a maximum yield of 62 to 63% of sec-butyl acetate at 100°C. With sulfuric acid, 60% conversion of normal butenes and pentenes is achieved at 60°C [106]. The boron fluoride-hydrogen fluoride catalyst rapidly reaches equilibrium (within 0.5 h) at 100°C and yields 80% isopropyl acetate for the direct esterification of propene and acetic acid. In general, increasing the amount of catalyst up to about 10% increases the yield of esters as does the concentration of olefin in the reaction mixture. These variables must be balanced, however, against the increased polymerization which can occur at high concentrations of olefin and catalyst.

Ethers

Secondary and tertiary ethers can be formed by the direct alkylation of olefins with alcohols or phenols. This reaction is catalyzed by acid catalysts. The low cost of sulfuric acid makes it the most practical catalyst and it has been studied extensively [40]. The reaction proceeds as follows:



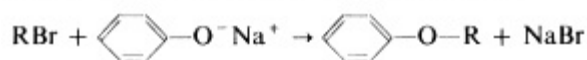
The reactivity of the olefin decreases as its molecular weight increases; thus isobutene reacts more favorably than 2-methyl-2-butene, and diisobutylene does not react at all. The reaction is further restricted to olefins containing tertiary carbon atoms since secondary olefins require higher temperatures and catalyst concentrations. Primary alcohols are more suitable than secondary alcohols while tertiary alcohols are found to react only slightly. In the presence of sulfuric acid the reaction proceeds most favorably at 60°C. Higher temperatures lead to alcohol dehydration and olefin polymerization, while lower temperatures give unacceptably slow reaction rates.

Phenols react with olefins to form alkyl aryl ethers in the presence of sulfuric acid [156]. Ether formation is favored by decreasing acid strength, temperature, and amount of catalyst relative to reactants. Alkylphenol form-

ation will be favored at the opposite conditions. A yield of 60% can be achieved at temperatures from -10 to 25°C in the presence of 0.5% by weight of sulfuric acid.

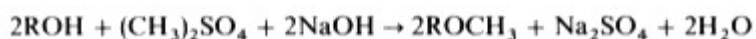
A reaction similar to the above is involved when the alcohol becomes the reactant instead of the corresponding olefin. In this reaction the alcohol is dehydrated in the process of forming the carbonium ion which alkylates with the remaining alcohol to form primarily symmetric aliphatic ethers. The reaction proceeds satisfactorily at 140 to 150°C when preparing diethyl ether commercially from ethanol in sulfuric acid.

Another method of preparing ethers is via the reaction of an alkyl halide with the alkali metal (sodium or potassium) salts of alcohols or phenols. This reaction, often referred to as the Williamson synthesis, involves the nucleophilic substitution of the halogen in the alkyl halide. The following reaction illustrates the formation of alkyl and aryl alkyl ethers [37]:



The Williamson synthesis is not suitable for reacting aryl halides or tertiary alkyl halides [109]. Furthermore, the reagents which can be used are generally expensive, hence this method of preparing ethers is of little industrial importance.

Ethers may also be prepared by reacting alcohols and phenols with dimethyl and diethyl sulfates in the presence of a metal hydroxide base. Aliphatic ethers as well as aryl alkyl ethers may be formed according to the following reaction in which R is an alkyl or phenyl group:



At less vigorous conditions (lower temperatures, less alkyl sulfate reagent) only 1 mol of ether is produced per mol of dimethyl sulfate [62, 94].

Alkylation of Nitrogen Compounds

The formation of amines and their derivatives by alkylation of ammonia and amines with various reagents is described in detail by Astle [12]. Ammonia as well as amines are bases owing to the presence of an unshared pair of electrons on the nitrogen atom. Thus these compounds are capable of reacting with reagents which are electron deficient. Amines may be prepared by alkylation of ammonia with olefins, carbonyl compounds, alcohols, and alkyl halides. Both aliphatic and aromatic amines may be prepared in this way. These products are mainly used as chemical intermediates in the manufacture of detergents, dyes, plasticizers, pharmaceuticals, antioxidants, and vulcanization accelerators [12].

Alkylation with Olefins

Alkali metals and their hydrides catalyze the reaction of olefins with ammonia and amines to form their N-alkyl derivatives [63]. Thus an approximately equimolar mixture of ethyl-, diethyl-, and triethylamines are obtained when ethene and ammonia are reacted at 175 to 200°C at 800 to 1000 lb/in². Higher molecular weight olefins may also be reacted; however, higher temperatures are required and lower yields are observed. Addition to the higher molecular weight olefins obeys Markovnikov's rule in that the amino group (NH₂) adds to the carbon with the fewest hydrogen atoms.

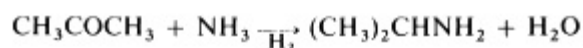
The alkali metals will also catalyze the reaction of amines with olefins to form secondary and tertiary amines. As the molecular weight of the olefin increases, disproportionation of the amines can occur. Thus when propene and n-butylamine are reacted, some di-n-butylamine is formed along with the butylisopropylamine.

The alkylation of aryl amines is an important reaction for the preparation of a number of dye intermediates. Olefin reagents, although not preferred, can be used for this purpose. The base-catalyzed reaction of aniline and ethene in the presence of sodamide yields 75% of N-ethylaniline at 275°C with lesser amounts (2%) of N,N-diethylaniline. With higher molecular weight olefins the reaction rates are much slower and the yields correspondingly lower. For example, at 330°C and 700 lb/in² only 6% N-isopropylaniline is formed when alkylating aniline with propene [24].

Nuclear alkylation of aromatic amines is difficult in the presence of an acid catalyst owing to the nucleophilic nature of the amino group. However, by initially reacting aniline with alumina to form aluminum anilide and subsequently reacting with olefin, nuclear alkylation of the aromatic amine can occur [33]. The mechanism is not clear and could involve either carbanion or free-radical-type reactions which lead only to ortho-substituted products. At 205°C and 600 to 800 lb/in², 86 % yield of N-ethyl-2-ethylaniline is obtained when alkylating N-ethylaniline with ethene.

Reductive Alkylation with Carbonyl Compounds

Ketones and aldehydes (carbonyl compounds) react with ammonia or amines in the presence of a hydrogenation catalyst (thus the terminology "reductive alkylation") and hydrogen to form primary, secondary, and tertiary amines. Reaction with ammonia will lead to primary amines:



A wide variety of aldehydes and ketones may be used provided these compounds can withstand the hydrogenation conditions without decomposition. Some secondary and tertiary amines will also be formed. A large

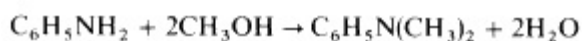
excess of ammonia will yield mainly primary amines. At a mole ratio of 2:1 of ammonia to carbonyl compound, primarily secondary amines will be produced, while an excess of carbonyl compound will yield mainly tertiary amines [12]. Replacing ammonia with primary and secondary amines will yield secondary and tertiary amines, respectively.

Catalysts for this reaction include Raney nickel [110]; palladium [12]; platinum black [87]; metal oxides of copper, chromium, and barium [163]; and metal sulfides of cobalt and rhenium [53]. Reaction temperatures range between 125 and 200°C at hydrogen pressures from 500 to 2000 lb/in².

Alkylation with Alcohols

Alcohols react with ammonia to yield mixtures of primary, secondary, and tertiary amines. Reactions are conducted in the vapor phase at temperatures ranging between 300 and 500°C and pressures of 100 atm in the presence of metal oxides of chromium, nickel, cobalt, aluminum, and others [12, 51]. Other catalysts fall mainly in the class of metal hydrogenation catalysts, such as Raney nickel and copper or supported platinum [12, 29, 58]. Alcohols ranging from methanol to dodecanol can be alkylated, with the yields of amines highest for primary alcohols since secondary, and to a greater extent tertiary, alcohols form olefins under these conditions.

The alkylation of aromatics with alcohols yields alkylarylamines. Thus dimethylaniline is formed by reacting aniline with methanol:



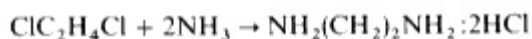
A commercial process for manufacture of dimethylaniline involves a liquid phase batch reaction in the presence of sulfuric acid as catalyst at 200°C [144]. Other catalysts designed to operate in the vapor phase and thus in a continuous mode include activated aluminas [39] which yield in excess of 95% dimethylaniline at temperatures ranging between 285 and 325°C and alumina-supported metal oxides which yield greater than 95% of the secondary amine, N-methylaniline. Raney nickel [131] and a Universal Oil Products nickel catalyst [25] will also catalyze the reaction.

Alkylation with Alkyl Halides

A mixture of primary, secondary, and tertiary amines is obtained by reaction of alkyl halides with ammonia. The reactivity of the alkyl halides decreases in the order iodides > bromides > chlorides. Commercially, however, the chlorides are in more common use owing to their greater abundance. The reaction is useful only when the products can be easily separated because of widely different boiling points. This is the case in general for alkyl halides containing three or more carbon atoms. Alternatively, the selectivity of the reaction can be altered to produce the various amines by adjusting the concentration of the alkyl halide

and ammonia. A large excess of ammonia, for example, will favor formation of the primary amines and vice versa.

An industrially significant application of this reaction is in the manufacture of ethylene diamine according to the following reaction [14]:



At a reaction temperature and pressure of 100°C and 90 atm, respectively, 70% yield of ethylene diamine is obtained, with the remainder being equally useful and easily separated polyethylenepolyamines.

Alcoholic solutions of ammonia are used in many cases to promote the reaction. Thus pentyl chloride reacted with an ammonia/ethanol mixture at 160 to 165°C yielded a 3:2 ratio of primary to secondary pentylamines with little formation of tertiary amines [169]. The product in this reaction, as in the ethylene diamine reaction, must be reacted with caustic to free the amine from its hydrochloride [65].

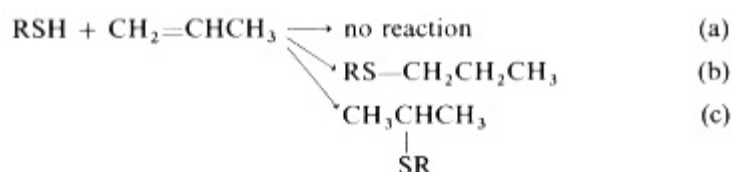
Alkylarylamines can be formed by reaction of arylamines and alkyl bromides; alkyl chlorides are not sufficiently reactive. Thus ethylaniline may be prepared at reflux temperatures by reacting aniline with ethylbromide. Mixtures of secondary and tertiary amines are formed; however, conducting the reaction in an excess of arylamine will suppress tertiary amine formation.

Alternatively, alkylarylamines may be formed by reaction of an aryl halide with alkylamines. A catalyst is required for this reaction because of the low reactivity of the aryl halide. At a temperature of 215°C, methylaniline is prepared from a 1:5 mole ratio of chlorobenzene and methylamine in the presence of cuprous chloride as catalyst under a pressure of 1000 lb/in² [64].

The reaction of alkyl halides with tertiary amines leads to the formation of quaternary ammonium salts which are soluble in water and are excellent cationic detergents. They are also useful as germicides [143] and algacides [28]. The most effective quaternary ammonium salts for these purposes are those containing one long-chain alkyl group (C₁₂ to C₁₈) and three small alkyl groups (C₁ to C₄). For example, 1-chlorododecane reacted with triethylamine and water at 155°C for 24 h will yield 64% of dodecyltriethylammonium chloride.

Alkylation of Sulfur Compounds

Mercaptans and thiophenols add to olefins to produce sulfides according to the following reactions:



With carefully purified reagents no reaction will occur [9, 79]. Ordinary samples of mercaptans, thiophenols, and olefins contain small amounts of peroxides which can catalyze the anti-Markovnikov addition (b), while in the presence of sulfuric acid catalyst, Markovnikov addition is observed (c) [71].

Thiophenol alkylation with olefin is also catalyzed by metals. According to the metal used, however, the addition can proceed according to or contrary to Markovnikov's rule. Thus reacting thiophenol and propene at 40 atm and 200°C in the presence of aluminum gives a yield of 77% of isopropyl phenyl sulfide, whereas in the presence of sodium at 50 atm at 200°C a yield of 72% of n-propyl phenyl sulfide is obtained [56].

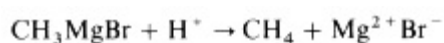
At high pressures and temperatures, hydrogen sulfide adds to alkenes to form mercaptans. Catalysts for this reaction include activated clays, sulfur, and metallic sulfides; the reactions occur according to Markovnikov's rule [79].

Nuclear alkylation of thiophenol is difficult due to the reactivity of the thiol group. However, boron trifluoride has been found to catalyze the alkylation of thiophenol and isobutene at 80 to 120°C to yield 60 mol% of 4-t-butyl thiophenol on the basis of thiol converted. Exclusively para substitution occurs. Other products result from alkylation of the S atom. Low yields of the ortho-substituted alkylthiol are obtained in alkylation of thiophenol with propene, and ethylation of thiophenol does not occur [15].

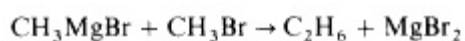
Alkylation of Metals

The alkylation of metals results in the formation of organometallic compounds which are useful as intermediates in other reactions (e.g., Grignard reagents), as polymerization catalysts (aluminum alkyls), or as in the case of tetraethyl lead as antiknock additives for automotive motor fuels. By far the most abundantly manufactured of these is tetraethyl lead. Its demand, however, may be reduced as a result of future requirements for lead removal from gasoline.

Bromomethane reacts with magnesium in the presence of dry ether to form methylmagnesium bromide, an organometallic compound referred to as a Grignard reagent. These reagents are salts of very weak acids, and hence they react with acids and even with water to form hydrocarbons [36].

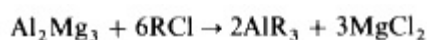


Grignard reagents also react with alkyl halides to form higher molecular weight alkylates:



Aluminum alkyls may also be formed by using Grignard reagents. Other less costly processes have been developed by Ziegler and others which involve one of the following reactions.

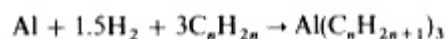
Aluminum-magnesium alloy with an alkyl halide at 30 to 170°C [172]:



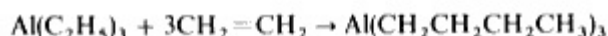
Olefin addition to aluminum hydride [142]:



or reaction between aluminum, hydrogen, and an olefin at about 120°C [171]:



Aluminum alkyls can catalyze the dimerization or polymerization of olefins. Thus at 200°C the following reaction may occur:



This product then reacts further with olefin to liberate the dimer and reform the catalyst [170, 145]:



Temperature, pressure, and contact time can be adjusted to obtain higher or lower molecular weight products.

Tetraethyl lead is manufactured at low or moderate temperatures according to the following overall reaction involving a sodium-lead alloy and ethyl chloride reactants [34, 132, 145]:



The products are steam distilled and unused lead is recovered.

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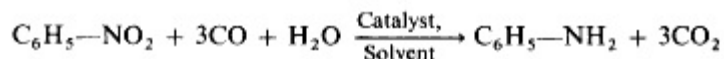
Amination

Lewis F. Hatch

Amines may be considered as ammonia derivatives in which one or more of the hydrogen atoms of ammonia have been replaced by an alkyl, aryl, arylalkyl, or heterocyclic group. Many different amination processes can be used to prepare amines both in the laboratory and by industry. In general, these can be classified as involving the replacement of a nonnitrogen containing group or the reduction of a group already containing a carbon-nitrogen bond such as the nitro group (RNO_2).

Reduction of Nitro Compounds

The reduction of various aromatic nitro compounds to amines is of considerable industrial importance because the required nitro compounds are readily available, easily reduced, and the primary amines thus produced can be converted to aromatic diazonium salts which are a versatile class of compounds. The preferred agent for the industrial reduction of nitrobenzene to aniline is iron in hydrochloric acid; in the laboratory tin is usually substituted for iron. Homogeneous rhodium-catalyzed deoxygenation of nitro aromatics by carbon monoxide in the presence of water results in the formation of the corresponding amine [21a]. The reaction with nitrobenzene is essentially quantitative:



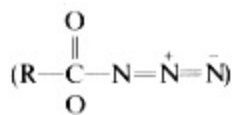
The catalyst is a rhodium carbonyl derivative in an aqueous base. Iron pentacarbonyl as a catalyst is equally effective.

Nitrobenzene and other nitro aromatics are catalytically hydrogenated both in industry and in the laboratory. The laboratory hydrogenation agent of choice is lithium aluminum hydride for both aromatic and aliphatic compounds. The industrial reduction of aliphatic nitro compounds is limited by their availability. An exception is the commercial production of alkanolamines from aliphatic nitro alcohols.

Reduction of Other Carbon-Nitrogen Containing Compounds

Other compounds which contain a carbon-nitrogen bond that can be reduced to a primary amine include nitriles (RCN), amides ($\text{(R—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—NH}_2\text{)}$), and

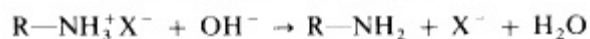
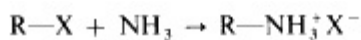
oximes ($R-CH=NOH$). Several different methods may be used to effect this reduction such as the use of lithium aluminum hydride, diborane, sodium in alcohol, and catalytic hydrogenation. Primary amines of low carbon number are prepared by the Hofmann



degradation of amides, from acyl azides by the Curtius reaction, and from carboxylic acids by the Schmidt reaction. The Gabriel synthesis is used to prepare pure primary amines from alkyl halides (RX). This synthesis involves the reaction between an alkyl halide and potassium phthalimide followed by treatment of the reaction product with a boiling solution of potassium hydroxide to produce potassium phthalate and RNH_2 .

Amination of Halides

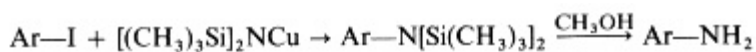
Amination of alkyl halides by reaction with aqueous or alcoholic solutions of ammonia is a general reaction for the preparation of amines. The initial product is the amine salt from which the amine is obtained by treatment of the salt with hydroxide ion:



A limiting factor in the use of this method for the preparation of amines is the formation of more than one class of amines (primary, 1° , RNH_2 , secondary, 2° , $RNHR$, and tertiary,

3° , $R-\overset{\overset{R}{|}}{N}-R$). The initially formed amine salt can react with ammonia to form the ammonium salt and the free amine. This amine can react with the alkyl halide to form a secondary amine which in turn can react with the alkyl halide to form a tertiary amine. This amination reaction gives the highest yield with primary alkyl halides and is of little value for tertiary halides because of the domination of the competing olefin formation reaction.

The low reactivity of aryl halides makes amination of little value in the production of aromatic amines unless the halide is activated by a nitro or similar group ortho or para to the halogen. Chlorobenzene, however, is aminated at high temperatures and pressures to produce aniline. A convenient laboratory method for the conversion of aryl iodides to amines consists of the reaction between the iodide and bis-trimethylsilylamidocopper [26]:



The bis-trimethylsilylamidocopper is prepared in situ from hexamethyldisilazene, *n*-butyllithium, and copper(I) iodide. Aryl bromides can also be used but the yield is lower.

The amination of aromatic compounds such as halides, phenols, and sulfonic acids has been reviewed by Nara [38].

The reaction between α -haloacetic acids and ammonia in the presence of dimethylsulfoxide has been reported for the preparation of α -aminoacetic acids [22]. Amination of halides has also been used to introduce the amine group into chloromethylated polystyrene [25]. The second-order kinetics of the amination reaction between butylamine and both chloromethylated polystyrene and benzyl chloride was studied in *N,N*-dimethylformamide and in dimethylsulfoxide. The entropy, enthalpy, and free energy changes for the aminations were calculated. Ethylene and ethyl iodide have been telomerized to give alkyl iodides which were aminated with ammonia to give C₂ to C₁₈ amines [35].

Amination of Alcohols

The amination of alcohols, especially methanol, is a well-established industrial method for the production of aliphatic amines [19, 20]. An extensive study of the reaction between methanol and ammonia to produce methylamines has been published by Serban [50].

The equilibrium constants and enthalpy of the amination of ethanol, 2-propanol (isopropanol), 1-butanol, and 2-butanol have been determined [45]. The equilibrium constants are highest with primary alcohols, and disproportionation of primary amines is favored more in the case of amines with nonbranched chains. The influence of pressure, temperature, and initial composition of the mixture on the equilibrium constant of primary, secondary, and tertiary amines and ethanol has been studied [46]. The equation for the kinetics of alcohol amination over an oxide catalyst has been derived based on a constant ratio, and the formulas were verified by the amination of *n*-decanol [29]. Equations also have been derived for the kinetics of the gas-phase catalytic amination of alcohols with amines by use of variable alcohol-amine ratios [30]. The equations were verified by comparing the calculated and experimental results for the amination of *n*-decanol over γ -Al₂O₃ at 250 to 350°C at 7.5 atm with an alcohol-amine ratio of 2.6 to 27.0.

The use of fused iron catalysts has been reported for the reaction between aliphatic alcohols and ammonia in the presence of hydrogen [24, 28]. Another catalyst that has been proposed is powdered nickel (100) containing chromium oxide (30) and kieselguhr (50) [16]. Use of this catalyst at 190°C gave an 83% yield of triisononylamine of 99.5% purity from isononyl alcohol. High molecular weight secondary alcohols (C₇ to C₂₉) are converted to the corresponding primary amines by their reaction with ammonia at 220 to 260°C in the presence of hydrogen at 2000 to 4000 lb/in² gauge over a nickel, cobalt, or

copper catalyst [23]. Primary and secondary amines are prepared in preference to tertiary amines in the reaction between butyl alcohol and ammonia in the presence of dehydrated crystalline aluminosilicate catalyst with pore sizes of 5 to 10 Å [17]. Apparently the small pores prevent the passage of trisubstituted amine products. Gumbrin (a clay which contains 40% organic material) activated by 30% sulfuric acid has been studied in respect to the amination of pentyl alcohol at 320 to 400°C [2]. Dimethyldodecylamine has been produced in a 95% yield by the reaction between dodecyl alcohol and dimethylamine at 360°C over a thorium sulfate on pumice catalyst [7].

Cyclohexanol has been aminated over gumbrin activated by sulfuric acid and gumbrin containing 8% iron oxide [3, 4]. The best yields (90% cyclohexylamine) were obtained with gumbrin containing iron oxide. Other catalysts for the amination of cyclohexanol include copper and zinc oxides [40]. When a platinum-carbon catalyst is used in the amination of cyclohexanol or cyclohexanone in the presence of an initially added quantity of hydrogen, the product is aniline (89%) along with 5% each of cyclohexylamine and benzene [6].

The amination of benzyl alcohol by ammonia and hydrogen over a sintered iron catalyst has been investigated in respect to such variables as pressure, temperature, and reactant ratio. The overall yield was 54% with a 4 to 1 ratio of benzylamine to dibenzylamine [27].

Amination of Phenols

The amination of phenol is an industrial process for the production of aniline. A typical process reported in the patent literature is the reaction between a phenolic compound with an aminating agent (ammonia) in the presence of hydrogen over a solid dehydrating catalyst and a hydrogenation catalyst. The use of $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ (8812) catalyst pelletized with powdered copper has been proposed [53]. When phenol is aminated with ammonia and hydrogen over this catalyst, the yield is reported to be greater than 90%. Aniline in high yield is also produced when phenol is treated with ammonia in the presence of a solid catalyst such as $\text{SiO}_2\text{-B}_2\text{O}_3$ [54]. Dicyclohexylamine is reported to be formed by the reaction of phenol with ammonia and hydrogen over a palladium-carbon catalyst [58].

Catalytic amination of the phenol-methanol system by ammonia over Al_2O_3 has been studied extensively [31]. The effect of ammonia pressure, temperature, phenol-methanol ratio, feed rate, and catalyst activity on the yield and composition of the aniline and methylated anilines and phenols are reported. An increase in ammonia pressure increases the total amination yield, decreases the total phenol content, increases the amount of methylated anilines and phenols, and decreases the amount of aniline and unreacted phenol. The effect of lithium ion additions on the activity of industrial aluminum oxide in the amination of the phenol-methanol system by ammonia under pressure has been reported [32]. The highest (69%) yield of aromatic amines was obtained at

450°C in the presence of 1% lithium hydroxide. This is a 1.5-fold larger yield than that obtained with lithium hydroxide-free Al_2O_3 . The mechanism of the catalytic effect of lithium hydroxide is discussed. It is suggested that it reacts with the protonic and aprotic acidity centers of the catalyst.

The naphthylamines (1- and 2-) are readily prepared from the corresponding naphthols by the Bucherer reaction. This reaction consists of heating (165°C) the naphthol with a concentrated aqueous ammonia solution saturated with sulfur dioxide. The amination takes place under the influence of the bisulfite ion in the reaction mixture.

Reductive Amination of Aldehydes and Ketones

The reductive amination of aldehydes and ketones to the corresponding amines has received appreciable study by industrial research laboratories with a concomitant number of patents. The more theoretical aspects of this method for the production of amines have also been the subject of research. Serban et al. [51] have investigated the reductive amination of acetaldehyde and acetone in the gas phase to obtain the corresponding mono-, di-, and triethylamines and mono- and diisopropylamines over a $\text{Ni-Al}_2\text{O}_3$ catalyst. Many parameters of the reaction were studied and compared with earlier work with methanol [50]. The influence of pressure, temperature, and initial composition of the mixture on equilibrium composition of primary, secondary, and tertiary amines has been determined for the reductive amination of acetone, butyraldehyde, and cyclohexanone [46]. Reductive amination of cyclohexanone over a nickel catalyst yields cyclohexylamine [33].

Nickel as a catalyst for the reductive amination of acetone [41], ketones [42], and cyclohexanone [39] has been studied in respect to various parameters. Nickel on aluminum oxide has been patented as a reductive amination catalyst for acetone [44], and an active Raney nickel catalyst is reported to be obtained if the normal preparation procedure is followed by a final washing with an alkali earth metal (preferably magnesium) salt solution [47]. Amines have been prepared from aldehydes and ketones over heated catalysts containing nickel, cobalt, and/or chromium activated by mineral acids. Yields were 90+% primary amines [1]. Secondary amines are prepared by reductive amination of aliphatic aldehydes with ammonia or a primary amine and hydrogen in the presence of a rhodium catalyst at temperatures from 0 to 125°C [12].

Secondary amines are also prepared by the reductive amination reaction of primary amines with aliphatic and alicyclic ketones over a palladium on carbon catalyst [59]. Methyl ethyl ketone with methylamine is reported to give an 88 % yield of N-methyl-sec-butylamine by this reaction. A typical method for the production of a tertiary amine is the reductive amination of cyclohexanone with diethylamine in the liquid phase with a catalyst containing 3% palladium on carbon [13]. An 82% yield of N,N-diethylcyclohexylamine was obtained.

Side reactions occur during the synthesis of isopropylamine from acetone by reductive amination [48]. The use of metal catalysts is accompanied by the thermodynamically favored hydrogenolysis to methane. This is true for nickel catalysts but not for copper catalysts. Aldol condensation is catalyzed by basic compounds present in the reaction mixture and leads to high molecular weight compounds which deactivate the catalysts. The condensation of ammonia and acetone leads to 2,4-dimethyl-5-ethylpyridine. The limitations these side reactions place on apparatus construction and conditions for the synthesis of isopropylamine are discussed by Richter and Pasek [48].

Preparation of α,ω -Diamines

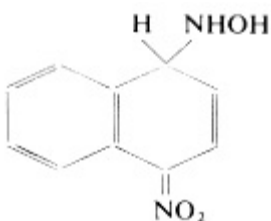
Reductive amination can be used to produce α,ω -diamines from α,ω -dicarboxylic acids. An iron catalyst has been proposed for the conversion of dicarboxylic acids to diamino compounds [10]. The efficiency of this catalysis is improved by the use of promoters such as aluminum oxide or thorium oxide. Adipic acid is converted to hexamethylenediamine over an activated cobalt catalyst [11]. Esters of dicarboxylic acids also can be converted to diamines by reaction with ammonia or a primary amine and hydrogen over a mixture of zinc and chromium oxides [18]. Both ϵ -caprolactam and ϵ -hydroxycaproic acid are aminated by ammonia and hydrogen over ruthenium on carbon or aluminum oxide to yield hexamethylenediamine [34]. Hexamethylenediamine also can be produced from ϵ -caprolactone by reaction with ammonia and hydrogen in the presence of Raney nickel or Raney cobalt [21]. The reported yield is about 40%.

Direct Ring Amination of Aromatic Hydrocarbons

Benzene and aniline can be aminated with ammonia in the presence of water in a temperature range of 300 to 500°C and a pressure range of 30 to 700 atm over nickel-nickel oxide catalysts containing strontium or magnesium and zirconium oxides [56]. The yields of aniline and phenylenediamines were $\sim 10\%$. Similar yields were obtained with benzene and toluene over strontium oxide-aluminum oxide or iron(III) oxide-zirconium oxide catalysts [55].

Higher yields of amines are obtained by use of hydroxylamine salts ($\text{HONH}_2 \cdot \text{H}_2\text{SO}_4$ or $\text{HONH}_2 \cdot \text{HCl}$). Biernacki reports the amination of toluene and ethylbenzene at 120°C in sulfuric acid containing vanadium pentoxide or ammonium molybdate gave only 2-aminotoluene-4-sulfonic acid and 2-aminoethylbenzene-4-sulfonic acid in a 40 % yield [8]. He also reported the production of 5-amino-2,3-dimethylbenzenesulfonic acid from o-toluene, 5-amino-2,4-dimethylbenzenesulfonic acid (37%) from m-xylene, and 3-

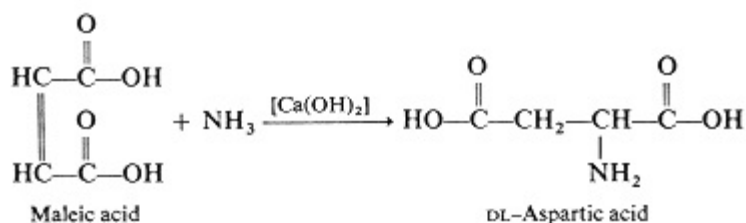
amino-2,5-dimethylbenzenesulfonic acid (23%) from p-xylene by the reaction of the respective xylenes at 105°C with hydroxylamine sulfate in concentrated sulfuric acid containing vanadium pentoxide [9]. Sulfonation was shown to be the initial step in these amination reactions. Amination of various alkylbenzenes at 100°C by hydroxylamine hydrochloride with aluminum chloride gave 48 to 70% yields of the corresponding amines [15]. The mechanism for the amination of 1-nitro-4-naphthylamine is suggested to involve the 1-nitro-naphthalene and the reaction product with the following intermediate [43]:



Metal-amine reductive amination of polynuclear aromatic hydrocarbons provides a new synthesis of novel secondary and tertiary amines. The conditions affecting this reaction were studied by Eisenbraun and co-workers [14]. Reductive amination takes place concurrently with, and at times in preference to, metal-amine reduction when an aromatic hydrocarbon reacts with sodium and a primary or secondary amine.

Amination of Unsaturated Compounds

The preparation of primary amines has been effected by the addition of ammonia to the carbon-carbon double bond of low molecular weight olefins. Ethylamine, for example, has been synthesized by the reaction between ethylene and ammonia over a palladium catalyst [37]. The heating of maleic anhydride, maleic acid, or fumaric acid with aqueous ammonia in the presence of alkali or alkali-earth hydroxides is reported to give a 98% yield of the amino acid, DL-aspartic acid [36]:



Various 3-aminopropionic acids are prepared by the addition of primary and secondary amines to the carbon-carbon double bond of various acrylic acids [49]. The reaction between vinyl chloride and ammonia in the presence of

a sodium-mercury amalgam under nitrogen for 1 h at 50°C is reported to give a 99% conversion of vinyl chloride to ethylenimine [57].

The amination of isoprene by ammonia at 150 to 200°C has been reported [52]. An increase in pressure, temperature, or reaction time favored formation of secondary and tertiary amines. Unsaturated 1,4-diamino compounds have been prepared by the reaction between conjugated dienes and tertiary amines in the presence of bromine at -40 to -30°C [5].

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Bromination and Bromine Compounds

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General Introduction

The chemical behavior of bromine is generally similar to that of chlorine. It has seven electrons in its outer shell and is a strong oxidizing agent, having an oxidation potential of -1.0652 V [1]. Thus bromine is a more powerful oxidant than ferric ion or dilute nitric acid, but weaker than oxygen or chlorine. Differences in the reactivity of bromine and chlorine arise from the larger size of the bromine atom, with a resultant smaller attraction of the bromine nucleus for electrons. Therefore, bromine is less reactive than chlorine, and brominated compounds tend to be less stable than their chlorinated counterparts. The bulkiness of the bromine molecule causes steric hindrance in some reactions.

Bromine attacks many of the metals and alloys commonly used as materials of construction, this action being accelerated by the presence of moisture. Since bromine has an affinity for water, it must be handled carefully to avoid picking up sufficient water to become highly corrosive to most metals. This corrosivity requires careful selection of materials of construction. Glasslined reactors are commonly used for brominations. Nickel, lead, and Monel Alloy 400 can be used for handling bromine if sufficient care is taken to exclude moisture. Tantalum is quite resistant to wet bromine and is often used for heat-exchange surfaces. Of the plastics, tetrafluoroethylene (Teflon) and polyvinylidene fluoride (Kynar) are usable over a wide range of conditions. Booklets available from bromine manufacturers offer detailed information and recommendations for selecting engineering materials. These booklets also describe in detail safe handling procedures for bromine.

Bromination processes are of importance not only for preparing specific desired end compounds (e.g., bromine-containing flame retardants), but also as a means of preparing reactive intermediates. Also, bromination often allows greater specificity than chlorination. This article reviews several commercially important applications of bromination. The first section treats the addition of bromine to unsaturated molecules. Subsequent sections discuss bromination of aromatic compounds and free-radical brominations. The final sections deal with processes that add bromine to a compound without employing bromine per se; e.g., hydrobromination.

Addition of Bromine to Unsaturated Compounds

Bromine reacts readily with unsaturated compounds in an addition reaction. Such reactions are usually run at low temperatures to avoid substitution reactions. Solvents are often used to avoid localized hot spots, but the reaction product itself often is most convenient for this purpose. The addition of bromine to an unsaturated compound is sufficiently rapid that a catalyst is usually not required. Ultraviolet radiation or higher temperatures may be used to accelerate the reaction, but side reactions increase with increasing temperature. The reaction mechanism may be either free-radical or ionic.

Among the more important commercial examples of bromine addition to unsaturated compounds are the manufacture of ethylene bromide, acetylene tetrabromide, 2,3-dibromopropanol, 1,2-dibromo-3-chloropropane, and hexabromocyclododecane. Typical manufacturing processes for compounds of this type are discussed in the following paragraphs.

Ethylene Bromide (1,2-Dibromoethane)

Ethylene bromide is the largest-volume bromine-containing organic chemical produced. Its major use is as a lead scavenger in gasoline containing alkyl lead antiknock additives. Ethylene bromide is made by the direct, uncatalyzed reaction of ethylene with liquid bromine.

The kinetics of this reaction have been reported by Williams [2] who found, in studies in glass, that the rate of reaction decreases with rising temperature and that water vapor accelerates the reaction.

Processes for the manufacture of ethylene bromide are reported in the literature [3, 4]. The following process description is based on the process described in Ref. 3. A schematic process diagram is given in Fig. 1. The main reactor consists of a glass column having a lower packed section and an upper reaction zone containing coils for heat removal. Liquid bromine is fed into the reaction zone and ethylene is introduced to the column below the packed

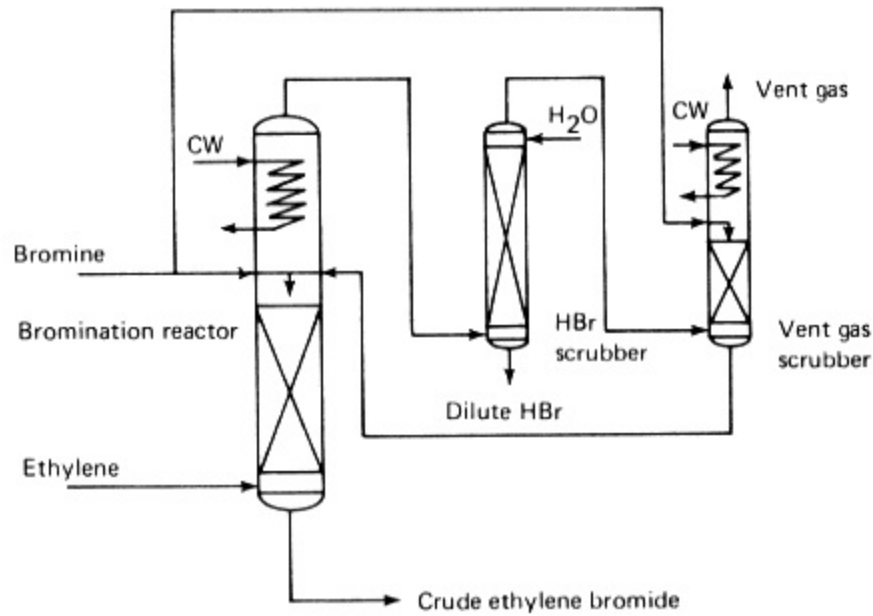


Fig. 1.
Ethylene bromide process.

section. Heat is removed through the coils to maintain a temperature of less than 100°C in the column.

The product ethylene bromide has a normal boiling point of 131.4°C [5] and so passes downward through the packed section and is discharged from the bottom of the column. The liquid product leaving the reaction zone contains a substantial amount of dissolved, unreacted bromine. As this mixture of bromine and ethylene bromide passes through the packed section, it comes into contact with rising ethylene, which both reacts with the bromine and strips the bromine from the product. At higher temperatures the reaction rate is lower and the action is mostly stripping. The vent gas from the reaction zone contains excess ethylene, HBr , and any inert impurities in the ethylene feed, but is substantially free of ethylene bromide and bromine, which are condensed by the cooling coils. A small stoichiometric excess of ethylene, 3% or less, is maintained. This excess ethylene can be recovered by passing the vent gas through a scrubber in which it is contacted with a portion of the bromine fed to the process.

The ethylene bromide product withdrawn from the reactor still contains some unreacted bromine and ethylene. These unreacted materials can be substantially eliminated by a photochemical treatment using wavelengths of 3800 to 5000 Å. Read et al. [3] indicate that a column 12 inches in diameter can produce up to 27 tons of product per day. Yield from the process is

substantially stoichiometric, with only slight losses in the vent stream. The product can be neutralized with an aqueous solution of soda ash, if desired.

Acetylene Tetrabromide (1,1,2,2,-Tetrabromoethane)

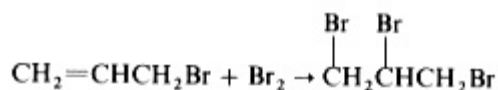
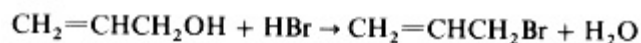
Acetylene reacts readily and completely with bromine to form acetylene tetrabromide. The reaction proceeds stepwise through the formation of dibromoethylene. No catalyst is needed, but the reaction is accelerated by visible or UV light. Major concerns in design of a process involving bromination of acetylene are safety (particularly with regard to introducing the acetylene to the reaction), heat removal, and product purification.

The reaction can be conducted batchwise by first adding the desired amount of bromine to the reactor and then establishing a flow of acetylene below the surface of the bromine. In one version of the process [6], the reaction is conducted in the presence of water, which is allowed to reflux, thus removing the heat of reaction. The reaction is terminated with a slight excess of bromine in the reaction mixture to maximize bromination of dibromoethylenes. Use of water is not essential, but provision must be made for removing the high heat of reaction. The excess bromine can be removed by neutralization with a dilute aqueous base.

Bromination of Unsaturated Alcohols

The manufacture of 2,3-dibromopropanol is an example of a process involving the bromination of a unsaturated alcohol. 2,3-Dibromopropanol is an intermediate in the manufacture of tris(2,3-dibromopropyl)phosphate, a widely used flame retardant.

When bromine is reacted with an unsaturated alcohol, there is the possibility of not only addition to the double bond, but reaction with the hydroxyl group as well. For example, Clemons and Overbeek [7] report that, in a batch reaction, up to 15% of 1,2,3-tribromopropane may be present in the reaction product when bromine and allyl alcohol are reacted in addition to the major product, 2,3-dibromopropanol. They report the mechanism of the side reaction to be



with the hydrogen bromide being produced by some minor side reaction, even when specially dried alcohol is used. Other by-products, such as brominated alcohol ethers, are also formed. Separation of some of these by-products from the desired product may be quite difficult; e.g., the boiling point of 2,3-

dibromopropanol is 219°C, while that of 1,2,3-tribromopropane is 219 to 221°C. Obviously, avoiding the formation of these by-products is desirable to maximize yield and to simplify purification. Several methods have been reported in the literature. Typically, these methods involve the use of a diluent, with simultaneous addition of the reactants over a period of time, in order to minimize the concentration of the reactants.

The formation of 1,2,3-tribromopropane may be suppressed [7, 8] and the yield increased by employing the reaction heel as a diluent. Thus a quantity of crude reaction mass from a preceding reaction is placed in a stirred reactor. Bromine and allyl alcohol are simultaneously fed to this reactor, maintaining a slight excess of alcohol and a reaction temperature of about 60°C. Crude product is taken off continuously while maintaining a constant volume in the reactor. The product is purified by fractionation, giving a yield of 80 to 85% and a product containing about 2% of 1,2,3-tribromopropane.

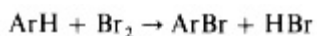
Other methods include the use of a catalyst or reaction promoter in addition to the diluent. Thus it was found [9] that high yield and purity can be achieved by using carbon tetrachloride as a diluent and calcium bromide dihydrate as a reaction promoter. In this process the reaction is run at 20 to 25°C, with simultaneous feed of reactants. Purification includes water washing and vacuum fractionation.

Methods [10, 11] that do not require fractionation to produce high-purity product have also been developed. One such process [10] involves conducting the bromination in the presence of an aqueous solution containing 45 to 65% lithium bromide. The product is only slightly soluble in the aqueous solution and can easily be separated from it. In this process, allyl alcohol and bromine are simultaneously added to a stirred solution of 60% lithium bromide solution at a temperature of 35 to 40°C. After addition of the reactants is complete, agitation is stopped and the bottom liquid phase containing the product is removed from the reactor. This withdrawn product contains a small amount of soluble and entrained lithium bromide solution, and makeup solution is added to the reactor to compensate for this loss. The addition of reactants to the lithium bromide solution is then repeated. The crude reaction mass is washed with water and dried by simple vacuum distillation. The product is reported to be very pure (99.8%) and the yield is high, about 95%.

Bromination of Aromatics

Aromatic compounds can undergo three types of reaction with bromine: (1) addition, (2) substitution on the side chains, and (3) substitution on the aromatic ring. The light-catalyzed addition of bromine across the double bonds of aromatic compounds is generally a slow reaction and is of little industrial importance. The bromination of aromatic side chains is normally a free-radical process and, therefore, it will be covered in a later section. This section will be confined to substitution on the aromatic ring, by far the most important type of aromatic bromination.

In the presence of suitable catalysts, bromine reacts with aromatic compounds to give aryl bromides and hydrogen bromide:



Suitable catalysts for nuclear brominations are Lewis acids, such as the halides of aluminum, iron, zinc, and antimony. The catalysts can be added as such or generated in situ from suitably dispersed metal powders. Iodine, alone or in conjunction with metal halides, has also been used as a catalyst for nuclear brominations. Bromination of some activated aromatic compounds, such as phenols, anilines, and aromatic ethers, can be accomplished without use of a catalyst.

Several factors affect the choice of solvent for aromatic brominations: compatibility with the catalyst, ease of product isolation and purification, economics of solvent recovery for recycle, possibility of by-product formation, efficiency of bromine utilization, and ecological considerations.

For uncatalyzed brominations of activated aromatics, polar hydroxylic solvents can be used and often are the preferred solvents. Water, alcohols, and acetic acid have been successfully used in the preparation of 2,4,6-tribromophenol. However, for partial selective bromination of phenols (as in preparation of p-bromophenol), nonhydroxylic solvents are more often used. In brominations that require Lewis acid-catalysts, hydroxylic solvents are unsuitable. Chlorinated and brominated hydrocarbons (carbon tetrachloride, methylene chloride, tetrachloroethane, ethylene bromide) are normally used for catalytic brominations. Chlorinated solvents have the advantage of lower cost and higher volatility. However, they can undergo the halide exchange reaction with hydrogen generated during brominations:



This side reaction can affect process economics by complicating solvent recovery and reducing overall bromine utilization.

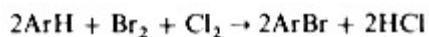
In bromination of deactivated aromatic molecules, special solvent systems might be required. Concentrated sulfuric acid and oleum have been used in the preparation of tetrabromoterephthalic acid and tetrabromophthalic anhydride.

Hydrogen bromide by-product of aromatic brominations must be recovered for recycle or utilized in situ to achieve the best process economics. When the manufacturing facility is located close to the bromine plant, the hydrogen bromide by-product stream can be easily returned for recovery of bromine values. When this type of process integration is precluded by geographic location of the bromination facilities, hydrogen bromide solutions can be neutralized with caustic and the resulting sodium bromide solution shipped to the bromine plant. However, the value of contained bromine is often offset by the freight costs involved. In bromination plants that generate sufficient volumes of by-product

hydrogen bromide, installation of a separate bromine recovery unit might be economically feasible.

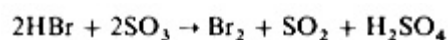
In situ regeneration of bromine from hydrogen bromide by-product is

practical in some aromatic brominations. Controlled quantities of chlorine are fed together with bromine to the reaction vessel to reoxidize the bromide to elemental bromine. Provided there is no loss of gaseous hydrogen bromide from the system, all the bromine values are utilized according to the following stoichiometry:



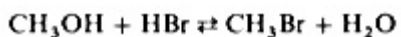
Preformed bromine chloride could also be used for the same purpose. The hydrogen chloride by-product is sent to an aqueous or caustic scrubber for disposal. Compared with conventional bromination, this type of process requires more elaborate feed controls to balance the bromine and chlorine feeds and to prevent loss of hydrogen bromide in the hydrogen chloride exhaust stream. Normally, it is difficult to achieve complete selectivity, and some chlorination of the aromatic substrate usually is observed. This can be a disadvantage when product purity is critical.

Improved bromine utilization is also obtained in brominations that are conducted in oleum. Here sulfur trioxide acts as an oxidant for hydrogen bromide:



Because of process difficulties, this approach is confined to polybromination of aromatics where product solubility problems may preclude the use of other solvents.

In special cases, bromine values from by-product hydrogen bromide can be recovered in the form of salable bromine compounds. For example, brominations conducted in methanol solvent can be adapted to coproduction of methyl bromide, a high-volume agricultural chemical:



However, because of the above equilibrium, complete recovery of bromine values is difficult to achieve.

Among the more important examples involving bromination of benzene derivatives are the manufacture of p-bromophenol, tetrabromobisphenol-A, hexabromobenzene, and tetrabromophthalic anhydride. Typical manufacturing processes for these compounds are discussed below.

p-Bromophenol

Although p-bromophenol is not a large-volume chemical at present, its preparation serves as a good example of partial bromination of an active aromatic compound.

The ortho and para positions of phenol are activated toward electrophilic substitution. As a result, the reaction of phenol with bromine can give both o- and p-bromophenols, as well as di- and trisubstituted compounds. If pure p-bromophenol is the desired product, brominations must be carefully con-

trolled to achieve maximum selectivity. Temperature and stoichiometry are important factors to be considered. Low reaction temperatures are needed to minimize formation of dibromophenol and to prevent accumulation of troublesome impurities arising from oxidative side reactions. Because it is rather difficult to separate 2,4-dibromophenol from p-bromophenol by distillation, dibromination must be suppressed by controlling the stoichiometry and by avoiding localized high concentrations of bromine in the reaction mixture. This can be done by using excess phenol, providing good agitation, and feeding bromine dissolved in the reaction solvent.

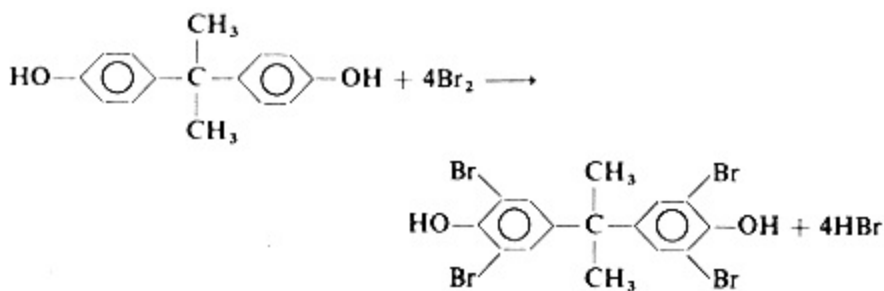
In a typical process for p-bromophenol [12], methylene bromide is used as solvent. A 45% solution of bromine in methylene bromide is added over a period of 4 h to a reactor containing 5% molar excess of phenol present as 24% solution in methylene bromide. The reaction mass is stirred during the addition and maintained at 18°C by cooling applied to the jacket. After bromine feed is completed, the reaction mass is stirred 1 h at 20°C. Hydrogen bromide, evolved from the reactor during the bromine addition, is passed into a scrubber containing water or caustic. Methylene bromide solvent is distilled off for recycle to the next batch. The crude product, obtained in 95% yield based on bromine, is purified by fractional distillation. A typical overhead product composition is 97.1% p-bromophenol, 1.5% o-bromophenol, 0.9% 2,4-dibromophenol, and 0.5% phenol. With more efficient fractionation it is possible to obtain p-bromophenol with 99% purity.

Distilled p-bromophenol frequently develops a reddish-purple coloration. Colorless p-bromophenol can be obtained by adding 0.5 to 1% water and sodium carbonate to the crude reaction product prior to batch fractionation.

p-Bromophenol, a low melting solid, is used as an intermediate in the manufacture of dyes, pharmaceuticals, and flame retardants.

Tetrabromobisphenol-A

One of the largest-volume aromatic bromine compounds, tetrabromobisphenol-A (TBBPA), is used as a flame retardant in epoxies, polycarbonate resins, unsaturated polyester resins, and polyurethanes. TBBPA, a white solid melting at 181 to 182°C, can be prepared by bromination of bisphenol-A in a suitable solvent system. No catalyst is required.



A number of solvent systems have been used in the preparation of TBBPA: glacial acetic acid [13], carbon tetrachloride [14], alcohols and alcohol-water

mixtures [1518], water-benzene, water-ethylene bromide [19], aqueous ethoxyethanol [20], and ethylene dichloride-water [21]. The choice of the solvent system is governed by such factors as the ease of product isolation, product purity requirements, recovery of by-products, utilization of by-product bromine values, and economics of solvent recovery for recycle.

In situations where methyl bromide is the desired by-product, methanol solvent is used. Typically, a slight stoichiometric excess of bromine (4.01 to 4.05 mol/mol bisphenol-A) is fed to an agitated, jacketed reactor containing a mixture of 40 wt.% bisphenol-A in methanol. The temperature in the reactor is maintained at 25 to 35°C (higher temperatures tend to give a colored product that is unsuitable for most applications). Because the reaction is strongly exothermic, bromine feed rate is normally determined by the heat-removal capability of the reactor cooling system. After completion of the bromine feed, the resulting slurry is heated at 60 to 65°C for 30 min. Methyl bromide (about 0.6 mol/mol bromine used) and some hydrogen bromide are given off during this postreaction period. After scrubbing with aqueous caustic, methyl bromide can be recovered by condensing in a refrigerated heat exchanger. The reaction mixture is then cooled to 30 to 35°C and pumped to a filter for recovery of TBBPA product. The solid cake is washed with water until free of hydrogen bromide and then dried in a vacuum oven at 40 to 45°C. Typical yields are 94 to 98% based on bisphenol-A used. Product purity is about 97%. Higher purity TBBPA can be obtained by conducting the postreaction treatment at a lower temperature for a longer period of time. Purification can also be accomplished by recrystallization from isopropanol.

The mother liquor contains aqueous methanol and dissolved hydrogen bromide. This necessitates corrosion-resistant filter and transfer lines. To recover bromine values, the filtrate is neutralized with caustic and stripped to remove methanol. The resulting sodium bromide solution is sent to a bromine recovery unit.

For economic reasons it is desirable to avoid the product purification step. Several processes capable of producing sufficiently pure TBBPA directly have been proposed. Bromination of bisphenol-A in aqueous ethoxyethanol [20] and in a mixed methylene chloride-water solvent [21] were shown to give highpurity TBBPA directly in yields of 93 to 96%. Generally, very close control of reaction variables is required to obtain TBBPA of adequate purity and low color.

In cases where recovery of bromine values from HBr or alkyl bromide by-products is not feasible, bisphenol-A can be brominated using bromine chloride or an equimolar mixture of bromine and chlorine [22]. In this case the by-product is hydrogen chloride, which can be neutralized with caustic for disposal. In general, the use of bromine-chlorine mixtures for bromination of bisphenol-A requires closer control of process variables and gives lower-purity products.

Hexabromobenzene

Multiple substitution of hydrogen atoms on the aromatic ring by bromine becomes progressively more difficult. For this reason the preparation of

hexabromobenzene requires higher reaction temperatures and longer reaction times. As a result, less volatile solvents such as tetrachloroethane [23], dibromoethane [24], and oleum [25] are commonly used. Iron powder and anhydrous ferric halides alone or in combination with iodine are the usual catalysts. Aluminum halides can also be used.

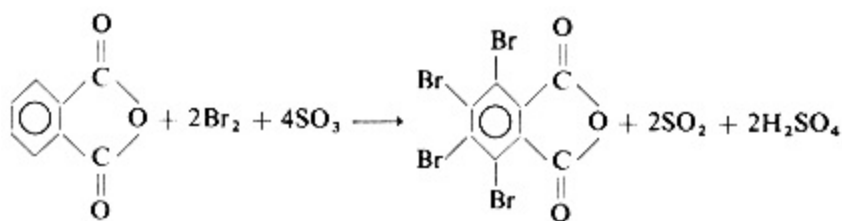
In a typical process [26] the reactor is charged with 1 part benzene, 18 parts tetrachloroethane, 0.03 part iron powder, and 0.03 part iodine. After the reaction mass is heated to 80°C, 6.9 parts of bromine (65% of theory) are added to the reactor in 10 h. The temperature is gradually raised to 143°C. The evolved hydrogen bromide is passed into a second reactor where it is reoxidized to bromine by mixing with chlorine. After condensation, the recovered bromine is fed to the main reaction mixture. The bromination cycle is finished in 15 h. After cooling to room temperature, the resulting slurry is filtered. Because unreacted bromine and dissolved hydrogen chloride are present, corrosion-resistant filters, slurry pumps, and transfer lines are required. The filtrate is recycled for use in the next bromination batch. The solid cake is washed with methanol. At this point the product still contains residual ferric bromide and must be further purified. This can be done by transferring the wet cake to a glass-lined vessel, resuspending it in dilute aqueous hydrochloric acid, and heating to reflux with agitation. After cooling, the slurry is filtered and the solid cake is washed with water and dried. The product is obtained as a white powder (mp 315 to 316°C) in 92 to 93% yield. An alternate purification method involves recrystallization from hot dibromoethane, followed by washing with methanol and drying at 50°C. The recovery of purified product is 93% based on the crude and can be as high as 99% if the mother liquor is recycled directly [27].

Hexabromobenzene is used as a flame-retardant additive for thermoplastic resins such as polystyrene, ABS, and polyolefins.

Tetrabromophthalic Anhydride

Tetrabromophthalic anhydride (TBPA) is used mainly as a reactive flame retardant in the manufacture of unsaturated polyester resins. A minor use is as an intermediate in the production of flame-retardant polyol comonomers for rigid polyurethane foam.

Bromination of phthalic anhydride is normally conducted at elevated temperatures in oleum. Sulfur trioxide present in the reaction mixture reoxidizes by-product hydrogen bromide to bromine, resulting in the following stoichiometry:

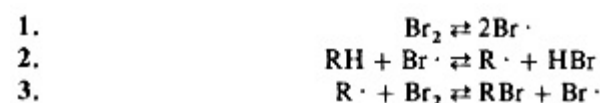


In a typical TBPA process [28], 148 parts of phthalic anhydride are mixed with 540 parts of oleum containing 65% SO₃, 0.5 part iron powder, and 0.1 part iodine. After the mixture is heated with vigorous stirring to 90°C, 330 parts of bromine are added slowly. The rate of bromine feed and the temperature must be carefully controlled in order to prevent excessive losses of bromine and sulfur trioxide from the reactor with the evolved sulfur dioxide. After addition is completed, the mixture is heated to 105°C and then an additional 40 parts of bromine are fed in. After the reaction is completed, excess bromine and sulfur trioxide are distilled off by heating the reaction mass to 140°C. After cooling, solid TBPA is filtered off, washed with 50% sulfuric acid to remove the iron catalyst, then washed with water and dried. The yield, based on phthalic anhydride, is 92 to 94%.

The product made by the oleum process generally contains occluded sulfuric acid (0.2 to 0.5%). This impurity often creates difficulties when the product is used in the manufacture of unsaturated polyester resins. The acid-containing TBPA can be purified by slurrying with dioxane, followed by filtration, water washing, and drying at 110°C [29].

Free-Radical Brominations

Bromination of saturated hydrocarbons, such as paraffins, cycloalkanes, and alkyl side chains of aromatics, occurs by a free-radical mechanism:

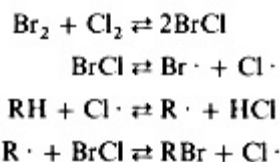


Dissociation of bromine molecules (Step 1) is needed to initiate the reaction. The initiation can be accomplished thermally, photolytically, by gamma radiation, or by the use of peroxide initiators. In Step 2 an organic radical is generated by abstraction of hydrogen from the organic substrate. Compared with chlorine, the bromine atom is less reactive, and the hydrogen abstraction step is endothermic, except in cases where the organic radical produced is stabilized by resonance. In bromination of alkanes, this has two consequences: reaction rates are relatively slow and the bromine atom exhibits high position selectivity. For example, in bromination of n-butane, secondary hydrogen atoms are replaced 82 times faster than primary hydrogens [30]. Therefore, bromination of linear alkanes gives almost exclusively secondary alkyl bromides. In bromination of branched alkanes, tertiary alkyl bromides are the predominant products.

Bromination of paraffinic hydrocarbons is a difficult reaction and thus is of little industrial importance. Because of the relative instability of alkyl-free radical intermediates, the kinetic chain lengths of the free-radical propagation step are very short at ordinary temperatures. For example, in the photolytic bromination of cyclohexane, the quantum yield is 12 to 37 at 100°C and only 2

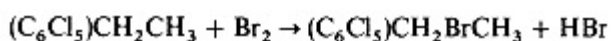
at 25°C [31]. Therefore, high energy requirements or high quantities of free-radical initiators are required to provide practical reaction rates and adequate conversions.

The use of bromine-chlorine mixtures (or bromine chloride) has been proposed as a way to overcome these difficulties [32]. Irradiation of a dodecane-bromine mixture with a mercury lamp while passing in chlorine at 20 to 50°C gave 58% conversion to bromododecane. The overall reaction here is apparently faster because hydrogen abstraction is accomplished by the more energetic chlorine atom:



Because bromine chloride exists in equilibrium with chlorine and bromine, some substitution by chlorine is to be expected. In fact, 4% conversion to chlorododecane was observed in the above example.

Bromination of aromatic side chains is a much faster reaction than free-radical bromination of alkanes. The reason for this is a much higher stability of the resulting free radical, which makes the hydrogen-abstraction step exothermic. Substitution occurs almost exclusively on the α -carbon atom. For example, photolytic bromination of pentachloroethylbenzene gives 91% yield of 1-bromo-1-ethylpentachlorobenzene [33]:



Most laboratory brominations of aromatic side chains are initiated photolytically. Organic peroxides can also be used as effective initiators [34]. Initiation of the reaction with X rays has also been reported [35].

In manufacturing operations, organic peroxides, such as benzoyl peroxide, are probably the most economical initiators. As in most free-radical chain reactions, chain-terminating poisons must be excluded. Oxygen does not retard the reaction [34]. For the optimum rate it is desirable to keep the bromine concentration low, to add the initiator in small increments or continuously, and to provide for an efficient removal of the by-product hydrogen bromide. The reaction is normally conducted at 80 to 100°C. Suitable solvents are carbon disulfide, carbon tetrachloride, tetrachloroethane, and benzene.

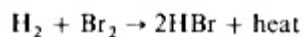
Bromination with Hydrogen Bromide

It is useful, in many cases, to introduce bromine through the use of hydrogen bromide; e.g., hydrobromination of olefins, reaction of HBr with alcohols, and

chlorine displacement. This section deals with methods for the manufacture of hydrogen bromide and with hydrobromination processes.

Manufacture of Hydrogen Bromide

Hydrogen bromide is prepared commercially by the direct gas-phase reaction of hydrogen and bromine:

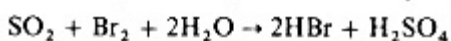
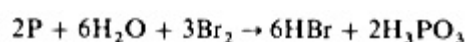


The reaction can be conducted noncatalytically at high temperatures by maintaining a self-sustaining hydrogen bromide flame within an enclosed burner [36] or catalytically at intermediate temperatures in a fluidized bed of activated charcoal [37]. Under nearly ambient conditions there does not appear to be any reaction, even in the presence of sunlight. The hydrogen bromide product can be used as formed, or it can be liquified by cooling for shipment in cylinders or absorbed in water to produce hydrobromic acid.

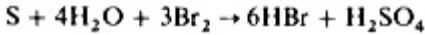
The noncatalytic reaction is conducted near the adiabatic flame temperature (1300 to 1400°C). The kinetics of the reaction and the properties of the hydrogen bromide flame have been widely studied and documented in the literature [3842]. Several burner designs have been proposed [36, 43, 44]. As with all combustion reactions, good mixing is essential to complete combustion in this process. Even with good mixing and a stoichiometric excess of hydrogen, trace amounts of bromine (as dictated by thermodynamics) will be contained in the combustion product. These can be removed with red phosphorus or activated charcoal if they are undesirable from the standpoint of subsequent processing.

The fluid-bed catalytic process is operated in the temperature range of 150 to 250°C. It has the advantages of good heat removal capability and allows for good mixing of the reactants. Also, the improvement in the process thermodynamics brought about by the lower reaction temperature leads to a product free of detectable trace quantities of bromine when an excess of hydrogen is used. In the design of either direct combination process, adequate safety precautions should be included to allow for the explosion hazards presented by hydrogen-bromine mixtures. Ignition temperatures in the range of 230 to 310°C have been calculated for such mixtures [42]. While there is some discrepancy in the experimental data, the combustible limits may be as broad as 20 to 95 mol% bromine in hydrogen.

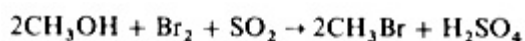
Other processes suitable for commercial production of hydrogen bromide include the reduction of bromine with red phosphorus, sulfur dioxide, or elemental sulfur [45, 46]. The overall reactions for these syntheses are:



and



Hydrogen bromide is also produced as a by-product in the bromination of hydrocarbons. The reduction of heavy metal halides with hydrogen or hydrocarbons [47] and the preparation of aqueous solutions of hydrogen bromide by distillation of alkali salt solutions following the addition of H₂SO₄ [48] are methods of less commercial significance. These processes are of interest since they form the bases for commercial processes for manufacture of methyl bromide that do not require external generation of hydrogen bromide. Methyl bromide is widely used as a soil fumigant. It can be made by the direct reaction of methanol and HBr, using ZnBr₂ or a tertiary amine hydrobromide salt as catalyst [49]. If HBr is unavailable, it may be readily generated in contact with the alcohol by several methods. One such process [50] involves the overall chemistry:



Yields are high, about 95%.

Hydrobromination of Olefins

Olefins can be hydrobrominated to introduce functionality into a molecule at a specific location. For example, hydrobromination of α -olefins can be conducted in such a manner that the resulting bromoalkane is almost entirely primary. This behavior allows considerable facility in tailoring molecules of various desirable configurations.

Markownikoff observed that, when a hydrogen halide is added to an olefinic compound, the halogen atom preferentially adds to the carbon atom having the fewest hydrogen atoms. Thus, addition of HI to propylene gives almost exclusively isopropyl iodide. This is usually referred to as ionic or normal addition. However, when certain free-radical initiators are present, hydrogen bromide exhibits "anti-Markownikoff" behavior, with the bromine adding preferentially to the terminal carbon of an α -olefin. However, even in the presence of free-radical initiators, hydrogen chloride does not exhibit anti-Markownikoff behavior to any significant extent. Among the free-radical initiators that can be used to promote anti-Markownikoff behavior are oxygen [51], organic peroxides [52], ozone or ozonide [53], and UV light. Anti-Markownikoff reactions are also favored by low temperature.

Several processes for the hydrobromination of olefins have been patented. A typical process is described in Ref. 53. A schematic process diagram is shown in Fig. 2. A portion of the olefin feed is contacted with ozone to form the ozonide. This ozonide-containing olefin is combined with the remainder of the olefin raw material to give an ozonide concentration of about 0.2 to 0.5 mol%. The olefin stream is then contacted with hydrogen bromide in a reaction system designed to provide efficient mixing and heat removal. One such system consists of a reactor equipped with a pump, heat exchanger, and recirculation loop. A high rate of circulation (about 50 to 100 times the feed flow rate) is

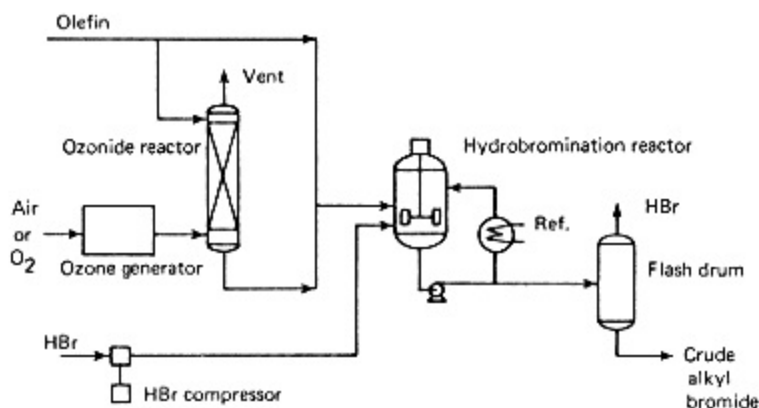


Fig. 2.
Olefin hydrobromination process.

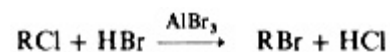
maintained through the recirculation loop to provide good mixing and minimize temperature. The reaction system is operated under a moderate pressure to promote solution of hydrogen bromide in the liquid phase. The temperature is maintained at 25 to 30°F. The ratio of primary to secondary bromide is reportedly as high as 85:1.

The crude reaction product is flashed to remove most of the excess HBr and is then washed with water or a dilute weak base to remove last traces of HBr.

A disadvantage of the process described above is the need for low temperature to achieve a high ratio of primary to secondary bromide. This low temperature requires refrigeration. Kessler [54] reports that in a similar reaction system the ratio drops to 32:1 at 50°F and 9:1 at 100°F. McCarty et al. [55] report that it is possible to achieve primary:secondary ratios of 25:1 or higher without the use of refrigeration by contacting the olefin and HBr in a rising-film reactor. This reactor maintains good interfacial mixing and mass transfer, while making available a large surface for heat removal.

Chlorine Displacement Via Hydrogen Bromide

Aliphatic chlorocarbons can be converted to the corresponding bromocarbons by reaction with HBr in the presence of a metal halide catalyst [56]:



This process can be used advantageously for converting chlorinated methane derivatives to their brominated methane analogs. An equilibrium reaction is involved, but it can be carried substantially to completion, with a relatively

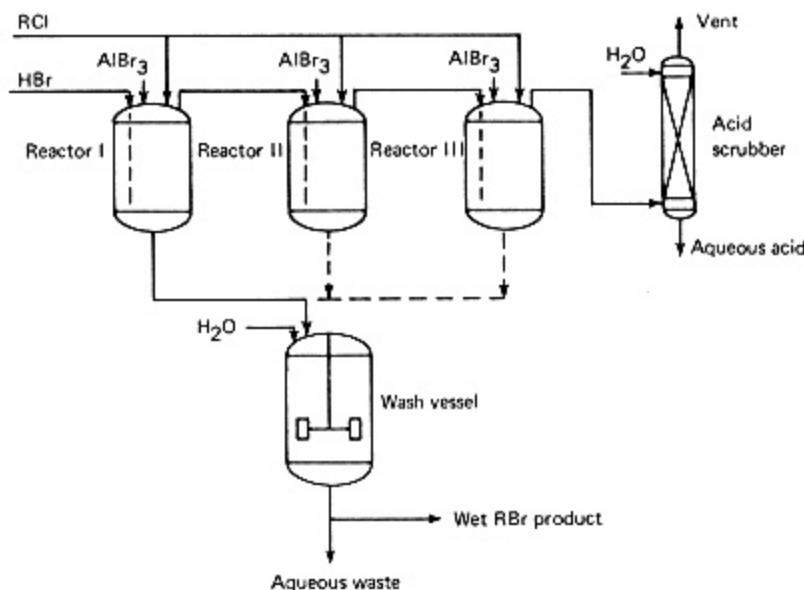
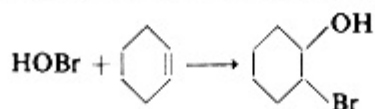


Fig. 3.
Process for chlorine displacement via HBr.

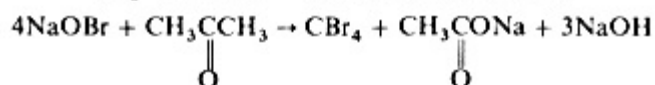
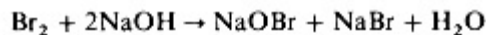
small excess of HBr, by the method described in Ref. 56 and illustrated in Fig. 3. Three reaction vessels are initially charged with a solution of catalyst in the starting chlorocarbon. Gaseous anhydrous hydrogen bromide is fed into Reactor I below the liquid surface. Gas evolved from Reactor I is passed into the liquid in Reactor II, and gas from Reactor II is passed into the liquid of Reactor III. The gas from Reactor III is principally HCl. When the contents of Reactor I are sufficiently converted to bromocarbon, the HBr feed can be diverted to Reactor II and the contents of Reactor I discharged for product recovery. Reactor I can then be recharged with chlorocarbon and catalyst and returned as the third vessel in the reaction series. The crude product is washed with water to remove the catalyst and dried. The yield reportedly is about 90%.

Bromination with Hypobromite

Hypobromous acid, generated in situ, can be added to olefinic double bonds to give 2-bromoalcohols. For example, reaction of cyclohexane with a sodium bromide-sodium hypochlorite solution in aqueous acetic acid gives 2-bromocyclohexanol in good yield [57]:



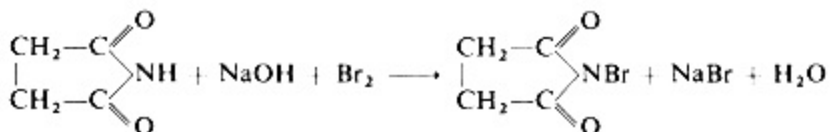
Perhaps a more important reaction from an industrial point of view is the preparation of carbon tetrabromide from acetone and sodium hypobromite:



In a typical procedure [58], bromine is added to an excess of 10% caustic solution at 0 to 10°C with agitation. Acetone is added to the resulting sodium hypobromite solution in small increments until the yellow hypobromite color is discharged. The product carbon tetrabromide can be filtered off or isolated from the reaction by extraction with a suitable solvent. Bromoform is often found as a minor coproduct. The crude carbon tetrabromide can be purified by recrystallization from ethanol.

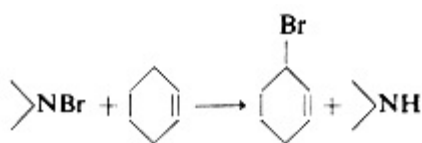
Brominations with Bromine Carriers

Bromine complexes and bromo imides are useful for conducting brominations where selectivity is of prime importance. The bromine carrier that has found the widest application in laboratory bromination is N-bromosuccinimide (NBS). It can be prepared by adding bromine to an aqueous alkaline solution of succinimide [59]:



A unique application of NBS is in free-radical allylic brominations. For example, 3-bromocyclohexene can be prepared in good yield by use of this

reagent [59]:



Free-radical initiators are needed. The most suitable initiators for allylic brominations are azobisisobutyronitrile and benzoyl peroxide. Best results are obtained by using solvents in which NBS is only sparingly soluble [60]. In homogeneous systems, addition of bromine to the double bond is a serious side reaction. Carbon tetrachloride, cyclohexane, and benzene are the most commonly used solvents. Succinimide formed in the reaction can be recovered for recycle.

Besides allylic brominations, NBS can be used as a brominating agent for aromatic side chains, saturated and unsaturated ketones also as an oxidizing agent for conversion of alcohols to aldehydes and ketones.

Dibromodimethylhydantoin, another bromo imide reagent, has also been used in applications similar to NBS [61].

Dioxane dibromide is a bromine carrier useful for selective bromination of olefinic compounds and monobromination of phenols, anilines, and heterocyclic compounds. It is also useful for bromination of aliphatic aldehydes and ketones. The reagent can be prepared by mixing bromine and dioxane with cooling, followed by precipitation with water.

Pyridine hydrobromide dibromide and various quaternary ammonium polybromides have also been used as brominating agents in situations where a controlled release of bromine during the reaction is desired. None of the bromine carriers mentioned here has achieved significant use in industrial applications. Because of processing costs, the use of these reagents is likely to be limited to production of less price-sensitive specialty products.

The contributions of G. M. Sulzer to the section on the manufacture of hydrogen bromide are gratefully acknowledged.

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Catalysis and Catalysts

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S. K. Goyal,
R. Ramakrishnan,
and S. Sunder

Catalysis plays a very vital role in the production of fuels and chemicals and in their transformations. Catalysis was actually a servant of mankind even before it was recognized by Berzelius as a special phenomenon in 1835, and it has been a subject of great interest in many scientific and engineering disciplines. It is of particular interest in petroleum refining. Almost all petroleum feedstocks are processed by catalytic reactions; for example, catalytic cracking, alkylation, isomerization, hydrocracking, hydrodesulfurization, reforming, polymerization, hydrogenation, and hydrotreating are used in making gasoline, jet fuels, kerosene, and fuel oils.

Catalysis was accorded its first world recognition in 1909 when Wilhelm Ostwald won the Nobel prize for his work. Three years later the same honor was bestowed upon Sabatier.

In view of the recent world energy crisis, which became sharply apparent as

a result of the Arab oil embargo of 1973 and subsequent OPEC activities, the significance of catalysis has become even more apparent and catalysis is rapidly becoming recognized as the principal means by which greater energy self-reliance will be attained by the United States and other industrialized nations.

This article contains a summary of the history of catalysis; a brief description of common terms and the fundamental theoretical aspects of catalysis; information on the different types of adsorption responsible for the surface reactions that take place on catalysts; kinetics and mechanisms of the surface reactions with particular reference to diffusion limitations; active site concepts, carbonium ions, and metal complexes; a description of methods of preparation of catalysts and their evaluation and testing; the important characteristics of catalysts such as activity, selectivity, stability, poisoning, and promotion; and a description of modern methods of measuring chemisorption on the catalyst surface and a brief description of the more important catalytic processes. The objective of this article is to give the reader a feel for the subject; detailed information can be found in the given references.

History of Catalysis

Catalysis, as a phenomenon, has been recognized on an historic timetable only relatively recently. Apparently the first catalysis to be carried out practically employed enzymatically catalyzed reactions in the form of wine and vinegar manufacture. Likewise, the preparation of soap is a very old practice. These reactions involve the catalytic conversion of sugar to ethyl alcohol, ethyl alcohol into acetic acid, and fat into a salt of fatty acid and glycerol.

During the latter part of the eighteenth century there was a great increase in expanding chemical knowledge, and it was only natural that the influence of outside substances on chemical reactions was investigated. Between 1780 and 1835 many significant experiments were reported which described the effects of outside agents on chemical reactions. These experiments involved reactions induced by acids in solution, reactions in the gaseous phase, and reactions induced by solids.

The means by which catalysts function was anticipated by Fusinieri who was the first to consider the relationship between adsorption and reaction enhancement by solids. Faraday, among others, appears to have been aware that adsorption of the reactants played an important role in the induction of reaction by a solid. Desormes and Clement suggested that oxides of nitrogen played a role in the oxidation of sulfur dioxide through the formation of an intermediate compound.

Many of the early experiments on catalytic action were done with materials which are important today as catalysts in the petroleum industry. Examples are strong acids, clays, and metals such as platinum.

Berzelius, one of the great organizers of chemical knowledge, was the first to see that the

many diverse phenomena of reaction enhancement observed by

previous workers were generally related. In summarizing the then recent chemical work during the year 1835, he proposed for the first time that the many different experimental observations and results on reaction induction were generally related in that chemical reactivity could be induced by outside agents without the agents apparently taking any part in the reactions. He called this general phenomenon "catalysis." In this generalization, Berzelius introduced the concept of a "catalytic force" and, in doing so, apparently ascribed to matter a special kind of property or force which was able to bring about chemical reactions. This far-reaching concept, while not pinpointing the exact function of a catalyst, did draw attention to the interrelationship of a large number of apparently unrelated experimental facts.

Following Berzelius and until the important contribution of Ostwald, the scientific aspects of catalysis marked time for the next 60 years. This does not mean that there was little interest in the field. Liebig and others attacked the idea, proposed by Berzelius, of a special kind of catalytic force. There was other activity, but the advance by Ostwald had to be accomplished before any real significant new advances were made in catalysis. During the 60-year period, the work of Wilhelmy and Bertholet stands out. Wilhelmy investigated the hydrolysis of cane sugar while Bertholet studied the hydrolysis of esters. Wilhelmy was the first to appreciate the time factor in chemical reactions. He, and later Bertholet and others, laid the ground work for chemical kinetics as we know it today. The concept of the importance of time in chemical reactions had to be advanced before the next step in catalysis could be taken.

In the latter part of the nineteenth century, Van't Hoff, Ostwald, Arrhenius, Helmholtz, and others developed the field of physical chemistry in which, for the first time, the newer concepts of chemistry were reduced to quantitative laws. About 1900, Ostwald recognized the true significance of the functioning of a catalyst. He defined a catalyst as a substance which alters the velocity of a chemical reaction without appearing in the end products. Ostwald's concept served to put catalysis on a measurable basis for the first time.

The science and technology of modern catalysis began at this time. Ostwald's succinct definition of catalysis dispensed with the Berzellian notion of a special kind of force being responsible for catalytic reaction. The advances in practical catalysis since that time have been such that today the chemical and petroleum-refining industries are based primarily on catalytic reactions.

Important Advances in the Science of Catalysis

Concept of active chemisorbed species	1922
Concept of active sites	1925
Role of carbonium ion in catalytic reactions	1937
Accurate measurement of surface area	1938

Role of diffusion in catalysis	1939
Role of solid state in catalysis by metals	1950
Dual functional catalysis	1953
Molecular sieves as cracking catalysts	1962
Shape-selectivity in molecular sieves	1966
Bimetallic reforming catalysts	1967

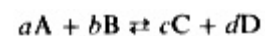
Important Advances in Catalyst Technology

SO ₂ oxidation	1900
Polymerization of olefins	1913
NH ₃ synthesis	1914
CH ₃ OH synthesis	1924
Fischer-Tropsch synthesis	1926
Coal liquefaction	1935
Catalytic cracking	1936
Alkylation of isoparaffins	1938
Catalytic reforming	1939
Catalytic reformingUse of Pt-Al ₂ O ₃	1949
Olefin polymerizationSteric regulated polymers	1953
Modern hydrocracking	1959
Hydrotreating	1960
Advances in homogeneous catalysis	1960

Definition of Terms

Energy and Equilibrium

The equilibrium concentration of the reactants and products is found by the free energy balance of the reaction. This has been explained as follows [1]: Consider a simple chemical reaction which can be written symbolically as



Here it is desired to convert substances A and B to substances C and D. The most important factors to be considered are: how much of A and B go to C and D? How fast does the reaction proceed? The amount of A and B that can go to C and D is determined by the energy difference between the reactants and products.

The energy we are concerned with is known as "free energy" and is usually represented by the symbol G. Any chemical reaction, if coaxed properly, will go to an equilibrium condition at which the free-energy difference ΔG between reactants and products approaches zero. In other words, the driving force of the reaction becomes zero. The

standard free-energy change, ΔG° , defines the equilibrium between reactants and products and is expressed arithmetically as

$$K = \frac{a_{\text{C}}^c a_{\text{D}}^d}{a_{\text{A}}^a a_{\text{B}}^b}$$

The activities (a_{A} . . . a_{D}) refer to equilibrium conditions in the reaction mixture and are defined as the ratio of the fugacity in the equilibrium mixture to that in the standard state; that is,

$$a_i = \frac{f_i}{f_i^\circ}$$

Further, if the gases follow the ideal gas law, the fugacities are equal to the partial pressures, and the equilibrium constant becomes

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

and the standard free energy change is

$$\Delta G^\circ = -RT \ln K_p$$

where R is the gas constant in cal/mole · degree, T is temperature in degrees Kelvin, p's are the partial pressures of reactants and products, and K_p is the equilibrium constant.

This equation states that the greater the downhill free energy, the higher the value of K_p and, in turn, the greater will be the yield of products at equilibrium.

These energy changes are of paramount importance in considering new reactions; for instance, the conversion of natural petroleum hydrocarbons into more desirable fuels and chemicals. Only in recent years have we had accurate and plentiful information about the energies of the simpler hydrocarbons which make up petroleum and many of the commercially important chemicals.

The values of free energies at different temperatures are found by the simple thermodynamic relation

$$G = H - TS$$

where H and S are enthalpy and entropy, respectively, at a temperature T°K. The data required for this kind of calculations are free energy of formation of each species as a function of temperature. These are available for most of the compounds in Circular C461 of the National Bureau of Standards [2]; if not, these are estimated by group contribution and/or bond energy methods given by Hougen et al. [3].

Reaction Rate

The rate of reaction is defined as the change in moles of a component, with respect to time, per unit volume of the reaction mixture. In catalytic reactions it is usually convenient to base the rate on a unit mass or surface area rather than the volume. The mathematical expression for the rate, r, is:

$$r = -\frac{1}{V} \frac{dN}{dt} \quad \text{or} \quad r = \frac{F}{W} \frac{dx}{dt}$$

where V is the volume of reaction mixture, N is the number of moles of one of the reactants, F is moles of feed, W is weight of catalyst, and x is the conversion.

There is a simple relation between rate of reaction and concentrations of

reactants, and it is expressed as

$$r = k(C_A^\alpha C_B^\beta)$$

where C_A and C_B are the concentrations of the reactants A and B, α and β are constants (α is the order of reaction with respect to A and β is the order of reaction with respect to B), and k is a rate constant and varies with temperature according to the Arrhenius equation

$$k = k_0 e^{-E/RT}$$

The Arrhenius equation applies only to elementary rate controlling steps, where E is the activation energy. Application of the Arrhenius law to catalytic reactions involving adsorption has been discussed by Laidler [4].

By definition the rate of a catalyzed reaction at any given temperature is different (usually greater) than that of the corresponding homogeneous noncatalyzed reaction. How the catalyst changes the rate of the reaction has been described by Oblad [1] with the help of the potential energy diagram, Fig. 1, involving chemisorption, reaction, and desorption.

In Fig. 1, E_h is the energy of activation for the homogeneous reaction to occur, E_2 is the activation energy for the catalyzed reaction, E_1 and E_3 are activation energies (usually small) of adsorption and desorption, respectively, e_1 and e_2 are heats of adsorption and desorption, respectively, and can vary between 0 and as high as 100,000 cal/mol. The small humps at the extremes represent van der Waals adsorption and may involve a small energy due to diffusion effects.

It can be said that the catalyst increases the rate of reaction by lowering the activation energy required for the reaction by forming an activated complex.

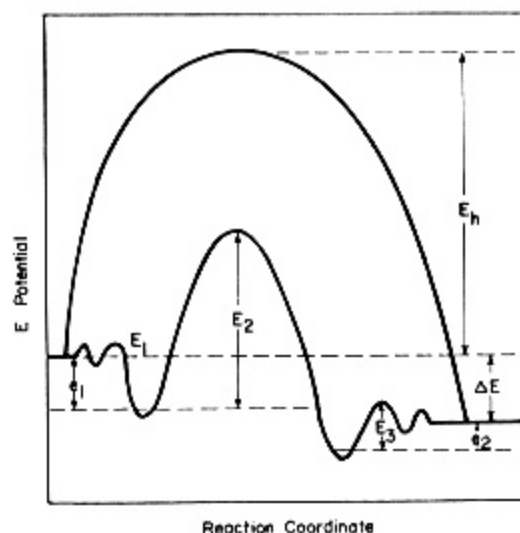


Fig. 1.
Energy diagram showing steps in a reaction.

Effectiveness Factor

The effectiveness factor, η , is defined as the ratio of the actual reaction rate, r_p , to the ideal unhindered reaction rate, r . Actual reaction rate is always less than the ideal one, due to heat and mass-transfer effects, and the ratio is of great importance for design purposes. Mathematically,

$$\eta = r_p / r \leq 1$$

The effectiveness factor can be evaluated if the value of effective diffusivity is known. Satterfield and Sherwood [5] have reviewed this method. Wheeler [6] writes $\phi_s = 3h$, where h is the Thiele modulus defined by Thomas et al. [7] as

$$h = L \left(\frac{2k_1}{rD} \right)^{1/2}$$

where L = length of the cylindrical pore

k_1 = rate constant

r = radius of cylindrical pore

D = diffusion coefficient

For the spherical catalyst pellet, ϕ_s is given by

$$\phi_s = R \left(\frac{k_v}{D_e} \right)^{1/2}$$

where R = radius of spherical catalyst pellet

$k_v = k_1 v =$ rate constant per unit volume

D_e = effective diffusivity

ϕ_s for pores of arbitrary shape has been given by Thomas et al. [7] as

$$\phi_s = R \left(\frac{k_1 \rho_p S_g}{D_e} \right)^{1/2}$$

where $\rho_p S_g$ = surface area per unit volume, and in these cases the shape of the pores is immaterial provided that the quantity $\rho_p S_g$ is a true measure of the surface area per unit volume. When there are no heat transfer effects, then comparison of the two reaction rates indicates the fraction of surface available for reaction which is given by

$$f_s = \frac{3}{\phi_s} \left(\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right)$$

For practical catalyst pellets, the same fraction can be taken simply as

$$f_s = \frac{\tanh h}{h}$$

where h is Thiele modulus and f_s may be taken as the effectiveness factor, η , for the isothermal process. Hence one may write

$$\eta = \frac{r_p}{r} = \frac{\tanh h}{h}$$

It is quite obvious that to obtain a correct rate for design work, the rate of the chemical reaction which is independent of in-pore diffusion effects should be multiplied by the effectiveness factor appropriate to the catalyst.

Homogeneous and Heterogeneous Catalysis

Most of the catalytic reactions can be classified as homogeneous or heterogeneous reactions. Both of these classes have different conditions and end effects. Though the great majority of industrial processes correspond to heterogeneous systems, still the study of homogeneous systems can shed much light on the nature of heterogeneous reactions. Catalytic reactions involve catalyst and reactants to produce products and unchanged catalyst in the ideal sense. The two systems, homogeneous, and heterogeneous, are differentiated as follows:

Homogeneous catalysis

1. Catalyst and components of reactants and products are in the same physical state and remain only in one phase

2. Catalyst is uniformly distributed throughout the system and the mobility of catalyst is same as that of the other components

3. Catalyst acts by its mass and the velocity coefficient is proportional to the concentration of the catalyst in the system

Heterogeneous catalysis

1. Catalysts and components of reactants and products are in different physical states or, if in the same physical state, they have different phases separated by a phase boundary

2. Catalyst is not uniformly distributed throughout the system and the mobility of catalyst is different (usually low) from that of the other components

3. Catalyst acts by its surface and the velocity coefficient is proportional to the catalyst area exposed for the reaction, the diffusion rate of the reactants to the catalyst surface, and of the products from the catalyst surface

Further, there are two types of homogeneous systems, namely homogeneous gas

catalysis which is accelerated through gaseous catalysts and homogeneous liquid catalysis in which a solute is used as catalyst. Many systems appear to be of a pseudohomogeneous character or actually heterogeneous because of the possibility of partial processes at the walls of the container, on liquid drops, or on dust particles. A detailed differentiation of the two systems with examples is described by Berkman et al. [8].

Carriers

A carrier is an inert material used as a support for the catalyst. Literally speaking, when the carrier changes the rate of reaction, it is no longer a carrier. Heinemann [9] has described carriers as "usually a major constituent of the catalyst, which serves as a base or support for the active component but which by itself is inactive for the desired reaction." But still one must keep in mind that a carrier is not at all an indifferent support for a catalyst. Carriers contribute the following functions to the catalyst:

1. Carriers are used in heterogeneous catalysis and a large surface area is needed in this kind of system. Carriers are the best and cheapest substitute for expensive metals such as platinum and palladium. Metal catalysts are deposited on a carrier's surface to give large surface area.
2. Carriers provide more even distribution of the catalyst.
3. Carriers preserve the fine dispersion of the catalyst, hinder aggregation by sintering, and increase the stability and life of the catalyst.
4. By preserving high surface area, carriers prevent the loss of activity.
5. High active surface area may result in a decrease in sensitivity to poisoning.
6. Carriers help in dissipating localized heat which prevents sintering of the catalyst.
7. The activity of a catalyst depends on the number of active centers and the distances between them which can be controlled with the help of the particular carrier.

To make the selection of a carrier, the following properties of carriers should be considered:

1. Physical properties

- a. Surface area
- b. Porosity
- c. Specific heat
- d. Heat conductivity
- e. Particle size
- f. Density
- g. Hardness, compressive strength, and attrition resistance
- h. Electrical properties
- i. Temperature stability

2. Chemical properties
 - a. Chemical composition
 - b. Structure
 - c. State of dispersion

3. Catalytic properties
 - a. Inertness or catalytic activity of the carrier
 - b. Dual nature of the carrier with the catalyst
 - c. Reaction stability

- d. Adsorption
- e. Ability to exchange ingredients
- f. Saturation capacity of the carrier

Carriers have not been classified since their nature and properties differ widely and their applications have always been specific. Innes [4] has classified them broadly as follows:

1. Low surface area nonporous
2. Low surface area porous
3. High surface area nonporous
4. High surface area porous
5. Miscellaneous type includes gels, cements, and fibrous materials

Different kinds of carriers have been used in the last century such as asbestos, pumice, kaolin clay, kieselguhr, active charcoal, bauxite, CuO, Cr₂O₃, AlCl₃, Fe₂O₃, MgCO₃, SiO₂, Al₂O₃, ZrO₂, and zeolites. A comprehensive literature has been compiled by Berkman et al. [8] describing the carriers for different reactions and catalysts.

Promoters

Promoters are also called activators. Promoters are added to the catalyst to promote or activate the catalytic reaction. Innes [4] has defined promoters in catalysis as "a substance added to the catalyst during the preparation in small amounts (usually less than 10%) which by itself has little activity but which imparts either better activity, stability or selectivity for the desired reaction than is realized without it." The above three properties, activity, stability, and selectivity, of the catalyst are improved upon by different types of promoters depending on their specific properties and applications. The promoters have been classified [4] according to their effects on the catalyst and the reaction. They are:

1. Structural promoters. Structural promoters stabilize the structure and retain the same surface area as the reaction proceeds.
2. Dual action promoters. This kind of promoter acts as a catalyst only for one step of the reaction system.
3. Electronic promoters. Promoters used to transfer electrons and holes generated as a result of reactions involving mostly metal surfaces and hydrogen.
4. Lattice defect promoters. These are added to increase the lattice defects where they increase the catalytic activity.
5. Adlineation promoters. Promoters to create an active interface between different

phases of the catalyst.

6. Selectivity promoters. Promoters to help carry out the desired reaction and to prevent the undesired reactions or further reactions.

7. Diffusion promoters. Promoters to lower the diffusion resistance of reactants and products by making high surface area-porous catalysts.

Accelerators

Accelerators are usually gaseous agents added to the feed stream and they act as promoters for the reaction. Accelerators are opposites of poisons. Accelerators perform the same function as promoters, such as to improve the activity, stability, and selectivity, and are classified [4] on the same basis, i.e., their effects on reaction are as (1) diluents, (2) decoking agents, (3) activity accelerators, (4) selectivity accelerators, and (5) depoisoning accelerators.

For economic reasons, the most commonly used accelerators are air, steam, and hydrogen.

Poisons

Small quantities of impurities in reactants which decrease the catalyst activity are known as poisons. Poisons slow down the reaction and eventually stop it altogether. Inhibitors are not considered as poisons. Reactants, products, and undesired products such as soot, coke, and wax are also not considered poisons. Poisons are only the substances present in reactants as impurities which destroy the catalytic activity.

Most poisoning is due to surface effect, and the strong bond formations make it permanent and irreversible. The catalyst can be reactivated from time to time. Some poisoning effects are reversible and poisons come into equilibrium with the catalyst, which can be removed easily by cleaning the reactants from the poisons, like passing dry gases in ammonia synthesis after the iron catalyst is slightly poisoned due to water vapor.

Poisons have been classified on the basis of their action into four categories:

1. Chemisorbed poisons
2. Selectivity poisons
3. Stability poisons
4. Diffusion poisons

Comprehensive reviews and examples of poisoning are given by Berkman et al. [8], Griffith et al. [10], and Innes [4].

Fouling

Fouling is the term applied to the formation of carbonaceous deposits (nonvolatile) on the catalyst in the course of many reactions of hydrocarbons and other organic substances. These deposits result from the reaction of

organic substances at higher temperatures. They are usually some form of carbon or heavy tars adsorbed on the surface and within the bare structure of the catalyst. These deposits eventually cover the surface, causing a decrease in the activity. These materials can be easily removed by regeneration, by combustion, or by reducing the catalyst in H_2 , if required. Studies of coke formation on $SiO_2-Al_2O_3$ have been done by Voorhies [11]. Oblad et al. [12] examined deposits formed over Cr_2O_3 during dehydrogenation of hydrocarbons.

Sintering

The surface of a catalyst often decreases during use due to crystal growth. This occurs more rapidly at higher reaction temperatures. This phenomenon is called sintering. Due to the rapid decrease in surface, there is an irreversible loss in activity of the catalyst. This is a common phenomenon in hightemperature catalysis. Much work has been done on sintering phenomena of different oxides and the reader may refer to books [13, 14] on sintering. The relation between activity of catalyst and the size of particles has been discussed by Thiele [15].

Inhibitors

The term inhibitor is applied to a substance which, when added in catalyst preparation in small amounts, results in lower catalytic activity, stability, or selectivity. The effect is opposite to that of a promoter. Storch et al. [16] have compiled the inhibition effects of Cl, S, and boric acid on Fe-Cu- Al_2O_3 catalysts in Fischer-Tropsch synthesis.

Activity

The performance of a catalyst is judged from its activity, selectivity, and stability.

The activity is generally thought of as a rate of conversion per unit weight, per unit area, or per unit volume of catalyst under specified conditions. Activity has been defined in several ways in the literature, depending on the reactions involved and the products desired. Activity of a catalyst could also be described as the percent approach to thermodynamic equilibrium of the reactants and products. Theoretically, the activity is directly related to the specific rate constant in the rate equation, but this is often difficult to obtain because of the many factors involved in a flow reaction. Some of these factors are diffusional effects, nonuniform pressure drops through a catalyst bed, and wall effects. The activity per unit volume of catalyst is of practical importance because process economics depend critically upon the voidage of the packed reactor. The activity of a catalyst depends on the surface area available for reaction, configuration of atoms on the surface or active centers, and chemical

nature of the catalyst. Activity of a catalyst is the most important criterion for its selection, and it depends on factors not well understood. There are no specific rules to increase or decrease the activity of catalysts, and one comes to know the activity of a particular catalyst only through experiments. Berkman et al. [8] have devoted a full chapter in their book to the activity of various catalysts and have described the methods of its measurement.

Selectivity

The catalyst does more than carry out a single reaction in either direction. Most of the catalysts accelerate more than one reaction simultaneously. A catalyst may catalyze a series of reactions starting with the formation of a single activated complex which may react to yield several products. Different kinds of active centers on the surface may adsorb, form different kinds of activated complexes, and react with other complexes, reactants, and even products to produce many other products. Selectivity of a catalyst is determined by the rate of desired reaction among other catalytic reactions. Different reaction rates during cracking of olefins were found by Greensfelder [17] on silica-zirconia-alumina catalyst. The selective reaction may be through a series of reactions, and different sites on the catalyst act in different ways, i.e., the catalyst sites which are capable of performing more than one function are known as polyfunctional catalysts. Polyfunctional catalysts choose the reaction path depending on thermodynamics and diffusional factors. For example, Heinemann et al. [18] showed that a bifunctional catalyst is capable of producing butane from heptane in one operation. The science of selectivity in catalysis is not sufficiently understood to predict the best catalyst to expedite one reaction and usually it is determined in the laboratory; however, the theoretical considerations involved have been summarized by Thomas et al. [7].

Stability

As mentioned earlier, catalytic reactions involve catalyst and reactants to produce products and unchanged catalyst in an ideal sense, but this is far from the case. The factors responsible for and important in stability are both physical and chemical in nature. Under the influence of several factors, the activity and selectivity can change with time, and this change leads to poor catalyst stability. Activity and selectivity of a fresh catalyst may improve in the early stages of use, but generally catalysts age, and they decrease with time until at some point the catalyst must be reactivated or replaced.

Catalyst stability is closely related to its physiochemical characteristics and the reactants chemistry. Generally, the activity of a catalyst is decreased over a long period of time due to poisoning, inhibition, sintering, and fouling. Thus the catalyst stability is influenced by many physical and chemical variables, and each particular catalyst system must be analyzed to determine specific causes for loss of activity and selectivity. It is also essential that the catalysts

have suitable porosity for diffusion and mechanical strength to resist attrition during transportation and loading in the reactor.

Some of the catalysts are regenerated (reactivated) easily by combustion or by chemical reaction depending on the causes for loss of activity in the catalyst. For example, coke can be burnt off by heating in air, or coke can be chemically reacted with hydrogen and steam.

Catalyst Preparation

Despite the widespread use of catalysts in petrochemical and other industries, catalyst preparation is more of an "art" than "science." Two catalysts of the same physical and chemical characteristics may have different activities and, therefore, the properties of the catalyst are not a sufficient guide in predicting its activity. The other properties which really make the catalyst active are determined by the total history of its preparation. In this part the guiding principles and techniques of preparing catalysts in the laboratory are discussed, whereas the specifics are found in patents and most of them are trade secrets of industry. General methods of catalyst preparation most often used are discussed in the following pages.

Impregnation

The process of impregnating an active component on an inert support is frequently the simplest and easiest method of making a catalyst. This involves contact of the solid support with a solution of the active ingredient as a soluble compound in water or some other solvent. Generally, impregnation of granular support involves the following steps:

1. Surface drying or cleaning, by heating in an oven or by evacuation, is done with a view to removing moisture from the support material. This moisture may hinder the penetration of the solution.
2. Some contact time between support and solution is required. Normally 30 min are sufficient for uniform wetting of support by an excess of impregnating solution.
3. Removal of excess impregnating solution, after adsorption, by filtration or centrifugation.
4. Drying, normally at 105 to 110°C in an air oven.
5. Calcination at temperatures sufficient to bring about further removal of solvent, and decomposition of salt, if required.
6. Pretreatment of catalyst with hydrogen or other gaseous substance to bring the catalyst to a state of activity, as required.

Supported powdered catalysts can be made in the same way. Catalysts prepared with powdered supports may be more active than those prepared

with granular supports. This is because of more efficient adsorption of the active component in the former than in the latter due to differences in particle size. Powdered catalysts will require pelleting for fixed-bed operation, but can be used in a fluidized bed when properly sized.

Impregnation methods usually result in nonuniformity of catalytic properties. This comes about by nonuniform evaporation of solvent within the pores of the support and capillary migration of the solution within the pore structure. These effects can be controlled by carrying out the drying in a controlled atmosphere of the solvent and/or by repeating the first four of the above steps by using a dilute solution until the desired composition is attained. The latter method gives more uniform distribution of active component on the support.

Coprecipitation

Catalysts prepared by coprecipitation are generally more active than those prepared by the impregnation method. This is due to more uniform distribution of the active component on the surface of the support in coprecipitation. In other words, the catalyst prepared by this method has a higher density of active sites than one prepared by impregnation. Therefore, coprecipitation methods are now employed extensively for the preparation of highly active catalysts. The following steps are usually carried out for coprecipitation of catalyst:

1. Preparing chemical solutions of desired pH
2. Mixing and stirring the solutions
3. Removing the precipitate by filtration or by centrifugation
4. Washing the precipitate to remove impurities
5. Drying the precipitate normally at 110°C in an air oven to vaporize moisture
6. Calcining at desired temperature to decompose salt
7. Pretreating to activate the catalyst

In the precipitation method, single or multicomponent catalysts are usually involved. In order to eliminate adsorbed or occluded impurities, the precipitation is carried out either by mixing a very dilute solution or by using ammonia or ammonia salts as precipitants along with the nitrate of the desired metal. Most often, nitrate salts of the desired cations are used because other salts such as chlorides and sulfates may act as poisons if retained in the final product. A higher degree of homogeneity is achieved by controlling the pH of the solution while coprecipitating. This is done by making one solution acidic and the other basic.

Gel Formation

Coprecipitation and gel formation methods are closely related, and gelation is considered a special case of coprecipitation. The process of gel formation is

dependent on the rate of precipitation and the lyophilic properties of the precipitate. Gelation produces maximum homogeneity in the catalyst. As mentioned already, gelation is a special case of coprecipitation. The steps in gel forming are the same as in coprecipitation except Step 3, where the gel is broken into pieces, if necessary.

Other Methods

Most of the catalysts in industry and in the laboratory are prepared by the three methods described above. Few catalysts with limited applications are prepared by special methods. Some of these methods are:

1. Wet mixing
2. Metal deposition
3. Thermal fusion
4. Chemical reaction
5. Leaching

In wet mixing, two or more components are mixed in a ball mill, dried, sized, and pelletized. Expensive metals are deposited on the carriers in ultrahigh vacuum at very high temperatures to prepare a very thin metal film for fundamental catalytic work. The results of metal films obtained by this method are quite reproducible and have been discussed by Wheeler [6] and Beeck et al. [19]. Thermal fusion of oxides is carried out by water-cooled electrodes in industry and by an induction furnace in the laboratory for small batches. Some catalysts are prepared by reacting two components or simply by decomposition of salts, oxidation of metals, and reduction of oxides to obtain a particular crystalline structure of the catalyst. Another chemical reaction which is carried out to increase the surface area and to decrease the amount of impurities is by leaching the catalyst with dilute acids.

Clean metal surfaces are necessary for the fundamental studies in heterogeneous catalysis. These are obtained by deposition or by stripping the surface of a pure metal from impurities, or prepared by high temperature degassing in ultrahigh vacuum, reacting the surfaces with chemicals, ion bombardment using inert gases, and by electric field desorption.

The general methods of preparing catalysts have been described above but, as stated earlier, this is more of an "art" than a "science" and researchers are advised to refer to particular catalysts and their preparation methods in the literature for details.

Catalyst Forming

Catalysts come in cylindrical, oval, and spherical shapes. The cylindrical catalysts have a ratio of length to diameter of less than 3:1 which prevents breakage. To get uniform

packing every time in the catalytic tower, the

catalyst is poured from a height so that each piece settles freely onto the bed. This is called natural packing and is the only reproducible method. The diameter of the vessel should be more than five times the size of the catalyst to obtain uniform reproducible packing [10] and to avoid channeling. The catalyst pellets must be strong to resist abrasion during transit, to resist loading and charging shocks, and they must have sufficient internal cohesion to remain intact during reaction. The pellet voidage is a very important consideration for the pressure drop across the reactor and the ultimate strength of the pellets to withstand the load in the catalyst bed. These have been related by Andrew [20].

Catalyst forming and pelletization are very important aspects in catalyst preparation for the reasons given above. There are different fabrication methods [21] for different materials depending on their properties and their applications. Specifically, alumina, which is most widely used as catalyst support, has different phases and hence different forming properties [22]. Catalysts are manufactured by pelletization, extrusion, and tumbling. In preparing the catalyst, the wall lubricant plays a very important role, and the optimum amount of lubricant, generally graphite or calcium stearate, should be used. If the lubricant is not sufficient, capping and lamination may occur, and an excess of lubricant weakens the structure of the catalyst [23]. Thus the catalyst must be formed by proper experience and knowledge.

Catalyst Fundamentals

Adsorption

When two immiscible phases are brought in contact, the concentration of each phase is frequently higher at the interface than in the bulk. This has been termed "adsorption." An interface is constituted by two phases, each being either a solid, a liquid, or a gas, with the only exception being a gas in contact with another, where one diffuses into the other. Mixing of gases goes to completion followed by a decrease in the free energy and an increase in the entropy of the system. Adsorption, on the other hand, tends toward an equilibrium concentration gradient, also with a decrease in the free energy. Depending on the nature of the bonding forces, it has been classified into two types: physical and chemical adsorption.

Physical Adsorption and Chemisorption

Surfaces of solids are usually in a state of stress under the influence of unstable forces of unsaturation. This can be readily balanced by adsorption of atoms or molecules on them. Physical adsorption occurs near the boiling point of a substance and involves heats of adsorption corresponding to those of condensation. Chemisorption can occur well above the boiling point of the adsorb-

ate and is usually more exothermic. In most cases the distinction between the two has been experimentally established. Thomas et al. [7] mention that physical adsorption involves forces of molecular interaction such as permanent dipole, induced dipole, and quadrupole attraction. Thus it is frequently referred to as van der Waals adsorption. Chemisorption entails rearrangement of electrons in the gas and the solid, with the formation of chemical bonds. There is evidence in the literature [24] that various types of chemical bonds ionic, covalent, and coionic are formed. Many diatomic gases dissociate before chemisorption. Langmuir [25] discovered as early as 1912 that both H_2 and N_2 dissociate on hot tungsten filaments above certain temperatures. Chemisorption involves heats of adsorption up to 100 kcal/mol whereas physical adsorption may evolve just a few hundred calories per mole. Exceptions to this rule are cited by Trapnell [24]. Carbon monoxide typically shows heats of less than 6,000 cal/mol (physical) and more than 20,000 cal/mol (chemical). However, in one case transition from chemisorption to physical adsorption shows no discontinuity at all. Hydrogen usually exhibits heats below 2,000 cal/mol (physical) and above 15,000 cal/mol (chemical), but it is chemisorbed below 3,000 cal/mol on some surfaces.

The rate of adsorption is often indicative of the nature of the process. Physical adsorption is rapid as it needs very little or no activation energy. Chemisorption is slower, but it can be accelerated by an increase in temperature like any activated process. Again, slow adsorption on a porous solid due to diffusion limitation may be mistaken for chemisorption and, likewise, fast chemisorption on a highly unsaturated surface to be physical in nature.

The other major differences are that chemisorption is very specific and changes the magnetic and electrical properties of the adsorbent surface; it is usually restricted to a monolayer and quite often is irreversible.

Physical adsorption is not important in catalytic action. The mechanism of any catalytic reaction can be envisioned as the formation of an activated complex on the surface of the catalyst. No catalyst promotes a reaction that is not thermodynamically feasible. However, it increases the selectivity for a particular reaction by lowering its activation energy. This is a direct result of preferential chemisorption. Selectivity may be dictated by steric hindrance effects, induction effects of neighboring atoms, polarity, acidity, basicity, and the nature of electron orbitals both in the catalyst and in the reactants. It is now generally accepted that chemisorption is the primary step in any catalytic process.

Adsorption Isotherms

An adsorption isotherm is described by an equation that relates the extent of equilibrium adsorption to the pressure at a constant temperature. Similarly, an adsorption-temperature relation at constant pressure is known as an isobar and a pressure-temperature relation at constant coverage as an isostere. Isotherms are the most common and convenient representation used to study adsorption.

Langmuir Isotherm

Langmuir studied adsorption of several gases on plane surfaces of glass, mica, and platinum [26]. His original theory requires that the adsorbed film be only a monolayer. Though subsequently he developed expressions for simple multilayer and dissociative adsorption on surfaces that are homogeneous, heterogeneous, or amorphous, only his homogeneous molecular and atomic adsorption isotherms find some use today. These are classic expressions and have led to the subsequent development of more sophisticated treatments.

Molecular Adsorption. Langmuir [26] said, "When gas molecules impinge against any solid or liquid surface, they do not in general rebound elastically, but condense on the surface, being held by the field of force of the surface atoms." If the fraction of the area covered by the adsorbate is θ at a pressure, p , then the rate of condensation can be written as $k(1 - \theta)p$ and the rate of evaporation as $k'(\theta)$ where k and k' are the forward and reverse rate constants, respectively, that are functions of temperature. At equilibrium these rates are equal and, therefore,

$$k(1 - \theta)p = k'\theta$$

therefore

$$\theta = \frac{ap}{1 + ap}$$

where

$$a = \frac{k}{k'} = f(\text{temperature})$$

Implicit in this derivation are the assumptions that the surface is energetically homogeneous, there are no forces of interaction between adsorbed molecules, and that adsorption is strictly limited to a monolayer.

Atomic Adsorption. If a gas dissociates into n atoms before adsorption, the probability of n adjacent sites being vacant for adsorption is $(1 - \theta)^n$, and that of n adjacent adsorbed atoms recombining to form the molecule is θ^n . Thus, at equilibrium,

$$k_1(1 - \theta)^n p = k_1' \theta^n$$

therefore

$$\theta = \frac{(ap)^{1/n}}{1 + (ap)^{1/n}}$$

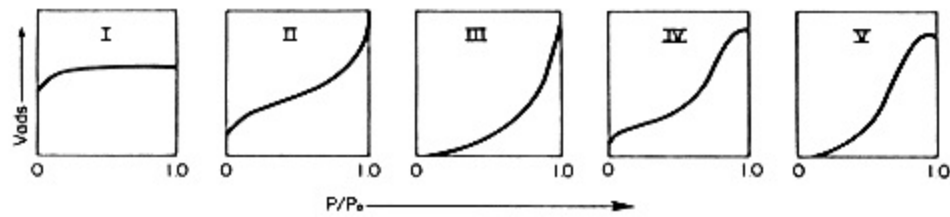


Fig. 2.
Five types of adsorption isotherms [4].

For diatomic gases,

$$\theta = \frac{(ap)^{1/2}}{1 + (ap)^{1/2}}$$

If i different gases adsorb without dissociation,

$$\theta_x = \frac{a_x p_x}{1 + \sum a_i p_i}$$

where a_i and p_i are constants and the partial pressures of the i th gas, respectively. Langmuir expression was found wanting in several respects in that none of the assumptions made ever really obtain in any adsorption process. The heat of adsorption usually decreases, with coverage, due the mutual repulsion of adsorbed entities. However, it is still used for some systems that conform to Type I adsorption; see Fig. 2.

Freundlich Isotherm

This is an improvement on the Langmuir equation in that it does not assume surface homogeneity but instead assumes that the adsorption sites are distributed exponentially according to the equation introduced by Zeldowitch and cited by Thomas [7] as

$$N(Q) = a \exp(-Q/Q_0)$$

where $N(Q)$ is the number of sites with a heat of adsorption Q , and a and Q_0 are constants. This is equivalent to saying that heat of adsorption falls logarithmically with coverage. This leads to the expression, $\theta = kp^{1/n}$ or

$$\ln \theta = \frac{RT}{Q_0} \ln p + \text{constant}$$

The main criticism against this expression is that it predicts infinite adsorption at infinite pressure. However, this expression was derived to be applicable only at low coverages.

Temkin Isotherm

If the heat of adsorption is assumed to fall linearly with coverage (instead of logarithmically as in the Freundlich isotherm), one obtains an expression such as

$$\theta = \frac{RT}{Q_0} \ln p + \text{constant}$$

Adsorption of nitrogen on iron at elevated temperatures seems to follow this equation [7].

The BET Multilayer Theory

The appearance of the BET multilayer theory [27] in 1938 was the most significant development in adsorption isotherm expressions since Langmuir first developed his monolayer adsorption theory. In the words of Ries [4], "It represents the first major effort to unify physical adsorption concepts as applied to the complete isotherm from the monomolecular region through the multilayer and capillary condensation regions to the saturation pressure." Brunauer et al. [27] aimed at developing essentially a two constant equation that will also fit an S-shaped adsorption isotherm where a Langmuir isotherm fails. They made the following assumptions:

1. The surfaces are energetically homogeneous and there are no forces of interaction between adsorbed species.
2. Adsorption can vary from zero to infinite layers on different areas of the adsorbent.
3. The heat of adsorption in the first layer is constant and those in all the layers above are also constant but equal to the heat of condensation of the adsorbate.

The area covered by a film, n layers thick, will be determined by its dynamic equilibrium by evaporation and condensation with the $(n - 1)$ th and the $(n + 1)$ th layers. The BET isotherm was derived as

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c - 1)p}{V_m c p_0}$$

where p is the system pressure, p_0 the saturation pressure, V the total volume adsorbed, V_m the monolayer volume, and c a constant:

$$c \approx \exp\left(\frac{H_1 - H_L}{RT}\right)$$

where H_1 and H_L are the heats of adsorption in the first layer and the heat of condensation, respectively. If we replace p/p_0 by x , this equation can be

rewritten as

$$\frac{1}{V(1-x)} = \frac{1}{V_m} + \frac{1}{V_m c} \left(\frac{1-x}{x} \right)$$

A linear plot of $1/V(1-x)$ against $(1-x)/x$ can be used to estimate V_m and c . If the area occupied by each adsorbed entity can be measured, then the surface area of the adsorbent can be calculated.

By about 1940, Brunauer et al. realized that there are five types of adsorption isotherms (see Fig. 2). Adsorption on porous solids shows hysteresis effects due to capillary condensation. Here the assumption of infinite layers is invalid. Modifications of the BET equation with the introduction of an additional parameter "n" have been successfully developed to cover these situations. The main reason for the celebrated acceptance of the BET equation is that it can fit all five types of adsorption isotherms. However, as the authors themselves point out, it is most reliable only in a p/p_0 range of 0.05 to 0.35. In spite of its limiting assumptions, it is still the single most commonly used method to determine the surface areas of catalysts.

Potential Energy Curves

It is a common practice to visualize adsorption as the state of minimum potential energy where the forces of attraction and repulsion between the adsorbate and the adsorbent balance each other. Polanyi formalized the theory in 1914 (see Adamson [28]): "The adsorbed layer resembles the atmosphere of a planet." Lennard-Jones developed power law expressions to represent the potential energy of an adsorbate as a function of its distance from the solid surface. A typical set of curves for a surface that has two types of (energetically different) sites is shown in Fig. 3. Point A represents weak

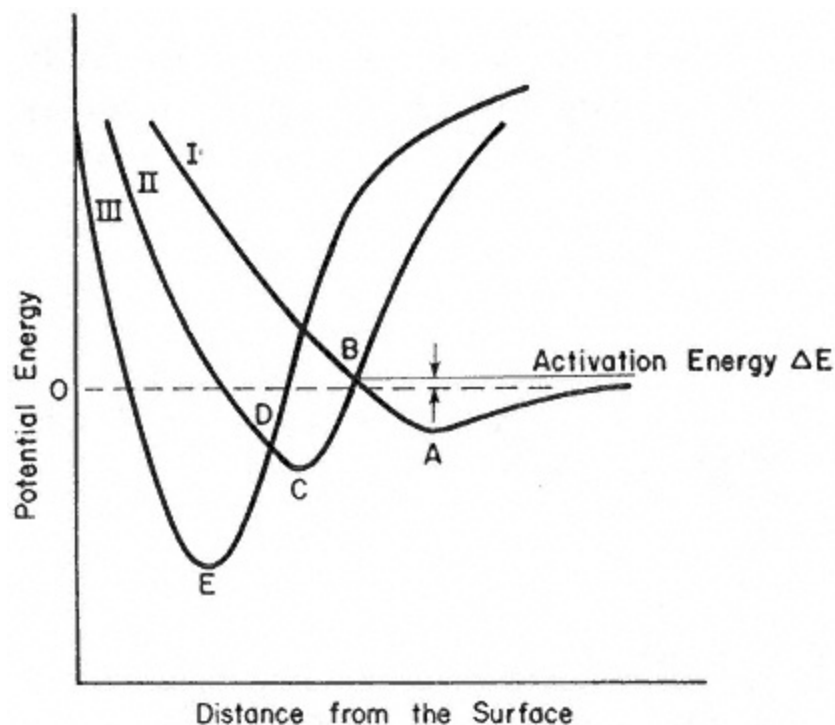


Fig. 3.

Potential energy curves for exothermic chemisorption on a heterogeneous surface.

physical adsorption. A molecule in this state can move along Curve I, dissociate at B, and be weakly chemisorbed at C, or it can move closer and be strongly chemisorbed at E. The activation energy for this process is shown in the figure.

Endothermic Chemisorption

The second law of thermodynamics may be written as

$$\Delta G = \Delta H - T\Delta S$$

Since adsorption is a spontaneous process, the change in free energy (ΔG) is negative. The change in entropy (ΔS) is also negative, because in most cases the adsorbate goes into a more ordered state as compared to its gaseous state. This is true even when it enjoys complete lateral freedom. Thus $-T\Delta S$ is positive, so ΔH has to be negative or, in other words, the process has to be exothermic. This is always true for physical adsorption. However, when a diatomic molecule dissociates, the two degrees of freedom of each atom represent a total of four instead of two degrees of freedom of a gas that does not dissociate on adsorption. The diatomic molecule has six degrees of freedom (3 translations, 2 rotations, and 1 vibration) in the gas phase. If adsorption induces mobility in the solid surface, the overall entropy change can be positive. When $T\Delta S$ is numerically greater than ΔG , then ΔH will be positive or the adsorption endothermic. This can be pictured as the adsorption of a molecule A_2 as $2A$ in Fig. 4.

Active Centers

The activity of a catalyst has long been known to depend on a number of factors such as the method of preparation, surface area, pore size distribution, acidity, size of reactant molecules, presence of impurities, temperature, and

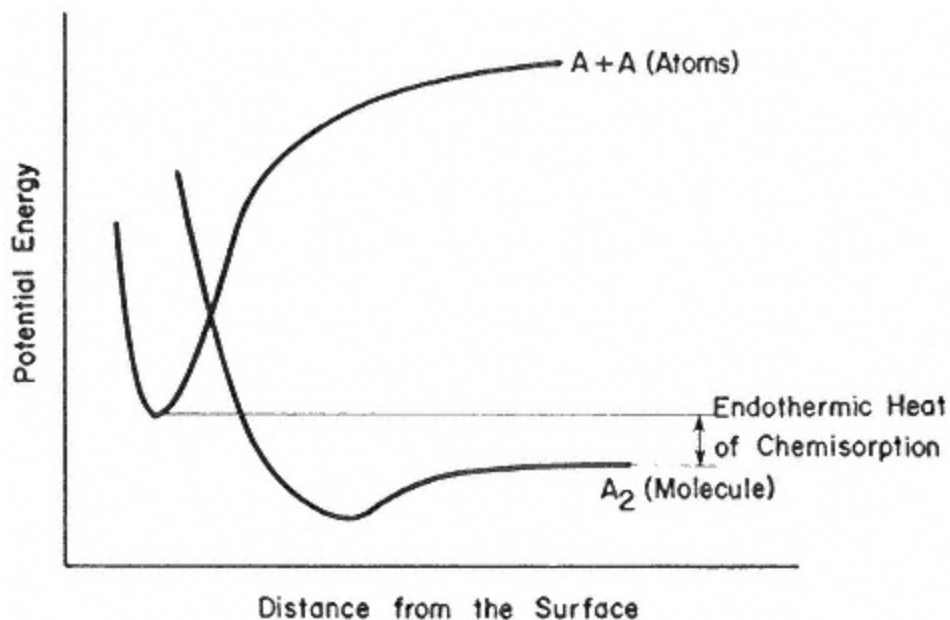


Fig. 4.
Potential energy curves for endothermic chemisorption.

pressure. As evidence grew, indicating surface heterogeneity with respect to adsorption and lack of uniformity of the catalyst surface, Taylor [29] proposed that surface atoms which are in a state of unsaturation are active centers for catalysis.

Early studies indicated that the heat of adsorption decreases progressively with coverage. This can be due to surface heterogeneity as well as due to the mutual repulsion between adsorbed molecules. Quite often, solids display the ability to adsorb different gases without displacing each other. Adsorption and desorption with radioactively labeled gases indicate energetically different adsorption centers. Nitrogen adsorption inhibits decomposition of ammonia on molybdenum [30] but it never stops it completely, even when it saturates the surface. Pease [31] observed that mercury, which reduces the activity of a copper catalyst for ethylene hydrogenation, inhibits hydrogen adsorption much more than ethylene adsorption. The ability of a promoter in enhancing catalytic activity or that of a poison in reducing it, even when these are adsorbed on only a small fraction of the total surface, suggests that a catalyst might owe most of its activity to a small percentage of its surface area.

Solids retain their shape by a balance of a combination of physical, ionic, and covalent forces, and can be stress-free only at the centers of perfect crystals. At a free surface the valence forces will be unsaturated and hence the atoms or ions are forced to assume abnormal bond distances. Taylor associated catalytic activity, therefore, with the edges, points, and cracks in the catalyst. More recently other types of defects have been recognized. These are typically cation or anion vacancies, local variations in stoichiometry in amorphous materials, or inclusions of foreign atoms with different valences in a compound. A typical example is a 12% Al_2O_3 -in-silica cracking catalyst where a trivalent Al ion is found to assume a four-coordinated structure of the SiO_2 . More generally, adsorption on different atoms of a compound, such as an oxide, can itself lead to energy heterogeneity and preferential adsorption of gases.

Geometric and Electronic Factors in Catalysis

Adsorption and catalytic studies on specific crystalline faces of highly purified metals, in the 1930s and 1940s, led researchers to believe that interatomic distances in these metal lattices may have significant influence on the activity of a catalyst. Carefully exposed crystal faces with regular spacings were found to be very active for some reactions. This is a significant point of departure from Taylor's concept of active centers.

Numerous investigations have been done on the relationship between catalytic activity and the electronic structure of solids. Activity has been associated with vacancies in the d-orbitals of metals. We shall discuss these in more detail under different classifications of solids.

Metals

Many metals are good hydrogenation-dehydrogenation catalysts and may be used pure or

supported on materials of large surface areas. Beeck et al. [19]

studied hydrogenation of ethylene on oriented and unoriented films of nickel and iron. The oriented films of nickel showed five times the activity of the unoriented films. The enhanced activity of oriented films was due to larger distances in the (110) plane of nickel and (111) plane of iron. Beeck and Ritchie [32] found that dehydrogenation of cyclohexane over (111) platinum faces was much faster than on (110) faces. This was in accordance with Balandin's multiplet theory which states that cyclohexane loses six hydrogen atoms in simultaneous adsorption at six adsorption sites. This has been questioned by many who have observed that it proceeds in three steps. Nevertheless, these are pioneering efforts in studying the importance of geometric factors in catalysis.

Electrons surrounding an isolated atom are confined to it in specific orbitals, as may be shown in the periodic table. However, in metals these are mobile, which makes metals good conductors. The extent of filling of the outer orbitals of an atom can be described in only statistical terms, namely, the relative times the electrons spend in different orbitals. The 3d and 4s orbitals in metals, for instance, are close energy levels, and therefore transitions between the two are relatively easy. Due to mutual repulsion of electrons, the d-orbitals prefer to hold five electrons with aligned spins or five pairs of electrons with opposed spins. The d-orbitals of transition elements are incomplete and their %d-character is a measure of their affinity for participation in dsp bonding. Beeck [33] found that activity for ethylene hydrogenation correlates well with the %d-character of a number of 3rd, 4th, and 5th period transition metals.

Trapnel [24] has described the nature of the surface bond in chemisorption by metals. The dipole moment at low coverages is indicative of the nature of the bond. Chemisorption of cesium, potassium, and sodium layers exhibits high values of moments, suggesting formation of monovalent positive ions at the surface. Covalent bonds are typical in adsorption of N_2 , H_2 , CO , C_2H_4 , and C_2H_2 on metals with partly filled d-orbitals. $Cu(3d^{10}4s^1)$ and $Au(5d^{10}6s^1)$, though with complete d-orbitals, chemisorb CO , C_2H_4 , and C_2H_2 because of the low energy required for their respective ds transitions. Some compounds containing atoms of Groups VA and VIA of the periodic table are strong poisons to metal catalysts. Some examples [20] are reactive electronegative species such as oxygen, sulfur, and halogens, and electron pair donors such as CO , pyridine, phosphine, H_2S , water, CS_2 , and ammonia. When a molecule like pyridine [C_5H_5N] forms a pyridinium ion [$C_5H_5NH^+$], the nitrogen no longer has a free electron pair to donate for coordination with a metal d-orbital and, therefore, it is not a poison.

Metal Oxides and Sulfides

The nature of reactions on metal oxides can be more complex than those on metals. The oxygen anions are active for chemisorption of acid gases such as CO_2 and SO_2 . Chemisorption of N_2 , HCS_2 , and O_2 is believed to be due to covalent bonding with the d-orbitals of the metal ions. Metal oxides are active in hydrogenation-dehydrogenation reactions that are typically catalyzed by metals; in cracking, isomerization, and cyclization that require acidic properties; and in dehydrogenation of alcohols that require basic

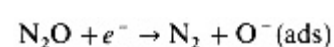
properties.

Oxides of the third period, Na_2O , MgO , Al_2O_3 , SiO_2 , and P_2O_5 , are insulators and exhibit progressively basic-to-acidic properties [20]. This is also true for oxides of the 4th, 5th, and 6th periods. Silica is acidic and its activity can be enhanced by the addition of alumina or magnesia. Some oxides are refractory and resistant to sintering. For this reason, alumina has been used extensively as a catalyst support for less stable but active phases.

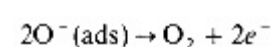
The electronic theory of catalysis generated interest in studying oxides that are semiconductors. According to the band theory, electrons surrounding the nuclei mostly reside in two bands separated by a forbidden energy gap. In insulators and stoichiometrically perfect compounds they occupy the valence band surrounding individual nuclei at low temperatures. Magnetic, photoelectric, or thermal activation can excite these electrons through the forbidden gap into the conduction band where they enjoy mobility between different nuclei. This gives rise to conductivity. Metals are good conductors due to the presence of electrons in the conduction band. Semiconductors, as the name implies, are intermediate between insulators and conductors. Structural defects, the presence of impurities, or nonstoichiometry due to an excess or deficiency of ions destroy the periodic nature of the solid. The net result is the establishment of electron donor levels just below the conduction band (n-type) or electron acceptor levels just above the valence band (p-type), both in the forbidden gap. This results in increased ease of electron transfer between the surface and the adsorbate and thus increases catalytic activity.

In some oxides such as ZnO , usually Zn is present in excess amounts which fit in interstitial positions. The valence electrons of this Zn^{2+} ion are loosely bound to it but can migrate easily to carry a current. ZnO is an n-type semiconductor. In some oxides such as NiO , Ni^{2+} ion vacancies or holes are common. To balance the charge, some neighboring Ni^{2+} ions have to assume a + 3 charge. Mobility of the holes due to physical migration of electrons gives rise to p-type semiconductivity. Similar cation deficiency can be introduced by substitution of some Ni^{2+} ions with Li^+ ions.

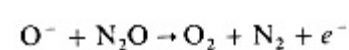
The importance of semiconducting oxides in catalysis is well illustrated by the N_2O decomposition studies compiled by Dell et al. [34]. This reaction is believed to proceed in two steps



and



or



The activity of semiconductors for this reaction follows the pattern p-type semiconductors

> insulators > n-type semiconductors. The slow step in the

overall reaction is oxygen ion desorption by losing electrons to the catalyst surface, and this is easiest on a p-type semiconductor.

Sulfide catalysts exhibit many of the properties shown by oxide catalysts. They are intermediate between metals and insulators, and they have semiconductor properties, too. They catalyze oxidation-reduction reactions as well as isomerization, cleavage, and dehydration [35]. Metal sulfides have been used extensively in hydrotreating coal liquids and petroleum crudes. Sulfur present in these raw materials is a poison for other catalysts and prohibitively expensive to be removed by separation processes. The capacity for ready adsorption of hydrogen and unsaturated hydrocarbons has also been significant in the development of metal sulfides as hydrogenation catalysts. Semiconduction properties in sulfides can arise just as in metal oxides. Excess sulfur in WS_2 produces p-type semiconductivity. The addition of NiS to MoS_2 increases its conductivity.

Strong Acids and Bases

Silica-Alumina. These are more complex structures than simple oxides. The activity of silica-alumina has been correlated with its acidity measured by reactions with inorganic bases [36]. The nature of the origin of acidity in silica-alumina has not yet been completely resolved. It arises because of amorphous substitution of Al ions for Si ions. To be a Bronsted acid, Al ions should replace some Si ions without altering the tetrahedral structure, where each cation is surrounded by four oxygen ions which are shared by two tetrahedra [37, 38]. To be a Lewis acid, aluminum should be in the octahedral six coordinated form, in which it is found frequently. Information in the literature indicates evidence for three points of view [39]: "(1) The alumina is present only as Lewis acids; (2) it is present only as Bronsted acids; (3) both Bronsted and Lewis acids are present." γ -Alumina, silica-magnesia, silica-zirconia, HF , BF_3 , AlCl_3 , H_2SO_4 , and H_3PO_4 are some of the other important acid catalysts. Acid catalysts are important in cracking, alkylation, polymerization, skeletal and double bond isomerization, and hydrogen transfer. An essential feature of all acid-catalyzed reactions is the formation of a positively charged carbonium ion intermediate. The product distribution is influenced by the relative stability of the carbonium ions which decreases in the order tertiary > secondary > primary. The literature on these is enormous and the reader may refer to Refs. 8, 40, and 41.

Base Catalysts. Base catalysts have not been studied as extensively as acid catalysts. The essential feature in this type is the formation of a negatively charged carbanion ion whose stability decreases in the order primary > secondary > tertiary. Thus alkylation of toluene with ethylene will give various isomers of methyl-ethyl benzene on acid catalysts and n-propyl-benzene on base catalysts. Base catalysts are active for polymerization, isomerization, alkylation, condensation, addition, and dehydrohalogenation reactions [41]. Oxides, carbonates and hydroxides of alkali metals and alkaline earth oxides are active base catalysts.

Molecular Sieve Zeolites

Molecular sieve is a term applied by McBain to certain highly porous crystalline aluminum silicate minerals. Molecular sieves are zeolites which are composed of metal aluminum silicates and have the properties of reversibly adsorbing large amounts of water, exhibiting ion exchange, and when dry reversibly adsorbing other gases and liquids. By the early 1950s a variety of zeolites had been synthesized, some being new materials not found to occur naturally. Still later other forms of molecular sieves were synthesized, and the end does not yet appear to be in sight even though about 44 species have so far been characterized. Breck and others have classified these into seven groups on the basis of the surface configurations of the framework [42].

Crystalline zeolites are usually prepared in the sodium form of the aluminum silicate. Preparation involves heating an aqueous solution or suspension of sodium hydroxide and source materials of alumina and silica at a temperature between 20 and 150°C or higher for periods from 15 min to many hours.

Zeolites are characterized by a three-dimensional framework of silica and alumina tetrahedra with the positive ions accommodated within the interstices. The positive ions are usually the monovalent alkaline metals (Na^+ , K^+ , etc.) or the divalent alkaline earth metals (Mg^{2+} , Ca^{2+} , etc.). The framework can take on many different configurations depending on how the tetrahedra are arranged and joined together and how much AlO_4 is substituted for SiO_4 . The tetrahedra are arranged so that sizable cavities exist within the structure. The cavities can be filled with water or other substances.

Zeolites have a number of properties which make them of real interest as catalysts:

Very large surface areas

Well-defined pore structure

Well-defined crystalline structure

Capability when properly prepared of retaining this structure at the temperatures and conditions of catalytic reactions

Variety of forms that exist through structural differences and ion exchange

Ease of preparation and modification

Reproducibility of the various forms

Catalysts must have pores large enough to allow reactant molecules ready access to the surface. For catalytic cracking, which is now by far the main use of zeolites as catalysts, only a few of the zeolites have the physical and chemical characteristics required. It was discovered that incorporating a relatively small amount of the zeolite (3 to 25%) in a matrix of silica, conventional silica-alumina, or clay produced a catalyst of very high

activity, very superior heat and steam stability, and attrition resistance. Still retained was the greatly improved selectivity of the zeolite catalyst. When the two catalysts are present together, because of the much greater activity of the rare-earth exchanged zeolites over that of conventional silica-alumina, a relatively small amount of sieve dominates the catalytic action.

Zeolites have been found to have activity for a large variety of carbonium reactions. These catalysts can be classified with other carbonium catalysts such as sulfuric and phosphoric acid, aluminum and boron halides, and silica-alumina. Accordingly, zeolites have definable activities for cracking isomerization, alkylation, polymerization, cyclization, and hydrogen transfer.

The similarities between zeolite and silica-alumina catalysts are summarized as follows:

1. Similarity of preparative details required to produce active catalysts. Upon removal of NH_4^+ from the structure by heat treatment, activity is developed in both silica-alumina and zeolites. Sodium is known to neutralize activity in both catalysts.
2. Both catalysts act through carbonium-ion mechanisms. Proof of this is shown in the cracking pattern obtained with pure hydrocarbons and gas oils.
3. Zeolite and silica-alumina catalysts have similar acid strengths differing in degree as shown by nonaqueous titrations and nitrogen-base adsorption and similarity of IR spectra of adsorbed pyridine. The amount of acidity as measured by pyridine adsorption is greater for zeolites (an order of magnitude or greater depending on the zeolite).
4. Activation energies for cracking are similar.
5. The need for small amounts of "bound" water for activity in both catalysts in the form of hydroxyl ions.
6. The promotional effect of carbonium-ion forming substances such as olefins.
7. Compatibility with silica-alumina as a matrix. The amount of zeolite in a silica-alumina matrix can be considered as a promoter for the native activity of the matrix.

There is one main point of dissimilarity between silica-alumina and zeolite catalysts. Exchange of sodium in the zeolites with di- and trivalent ions, particularly the rare-earth ions, produces very active catalysts. This does not appear to be the case with silica-alumina based on the data available.

However, active catalysts have been prepared containing multivalent cations. Furthermore, active clay catalysts are known to contain magnesium, and this has been said to be responsible for the higher yields and lower quality gasolines made with clay catalysts. For the zeolites it is clear that one of the main functions of multivalent cations is to stabilize the lattice.

Considering the detailed similarities between silica-alumina and zeolite catalysts, it can be concluded that the source of carbonium-ion activity in the zeolites resides, as with silica-alumina, in the acidic characteristics of the structure. Zeolite acidity depends on the nature of the cation present, the extent of ion exchange, the Si/Al ratio of the lattice, the heat treatment of the zeolite, and the amount of "bound" water present.

Accordingly, the acidity may vary from essentially zero to up to 14 or more times that of silica-alumina. Also, the distribution appears to be different, silica-alumina having a higher percentage of total acidity in its strong acid

range. The acidity is believed by most investigators to be both fully constituted Bronsted acids and potential Bronsted acids in the form of Lewis acids [39].

The reactions catalyzed by zeolites have been described in detail in Ref 43. These include hydrocarbon transformation reactions such as cracking, alkylation, dealkylation, and transalkylation, skeletal isomerization, positional and geometrical isomerization of double bonds, condensation of olefins to form dimers and telomers, and hydrogen redistribution.

Catalyst Testing and Evaluation

Surface Area, Particle and Pore Size Distribution

The knowledge of surface area and pore size distribution of a catalyst is vital to the understanding and development of any catalytic process. Solid catalysts for heterogeneous reactions are porous with internal surface areas that are several thousand times their external geometric area. However, all of the internal surface area is seldom active for catalysis. Activity can usually vary from being restricted to a minute fraction to all of the available area. The significance of measuring the surface area was first realized by Taylor in 1935. The method of surface area measurement as developed by Brunauer, Emmett, and Teller [27], in Emmett's words [4], "has been an important factor in the transition of catalyst preparation from an art to a science." The BET method has been used the world over ever since. It has been invaluable in attaining reproducibility in catalyst preparation, and in the comparison and correlation of properties such as activity, stability, and selectivity. A knowledge of the pore size distribution is helpful in determining accessibility of adsorption sites to various molecules. It is also important from the standpoint of diffusion effects and catalyst regeneration. Table 1 shows the kind of information that can be obtained by using some of the more common techniques of surface measurement, while a brief description of many of the available methods is given below. For any detailed information, the reader should consult Refs. 4, 7, 10, 24, 28, and 44.

Low Temperature Gas AdsorptionThe BET Method

Monolayer volumes of physically adsorbed gases can be calculated using gas adsorption isotherms. The surface area can be calculated if the area occupied by a single adsorbed entity can be estimated or measured. It is customary to assume hexagonal close packing of adsorbed species. Information on such areas is available from experiments or empirical formulas. Although Langmuir and Hüttig isotherms can be used for monolayer volumes of some systems, the BET equation with N₂ adsorption at -195°C has been used almost universally in gas adsorption measurements. It is excellent for solids with crevices and capillaries of large diameters ($>50 \text{ \AA}$) as compared to molecular dimensions. For surfaces with micropores, BET theory is valid only

TABLE 1 Comparison of Types of Surface Area and Particle Size Information Obtainable by Various Experimental Techniques Composed of Tiny Crystallites or Tiny Blocks of Amorphous Material (courtesy of Reinhold Publishing Co. [4])

Experimental	Total Surface Area	External Area of Particles	Particle Size	Particle Size Distribution	Size of Crystallites	Size Distribution of Crystallites	Size of Amorphous Blocks	Size Distribution Amorphous Blocks
Gas adsorbed, N2 at -195°C	Yes	No	No	No	Sometimes ^b	No	Yes	No
Sedimentation	No	Yes	Yes	Yes	No	No	No	No
Permeability	No	Yes	Yes	No	No	No	No	No
Light microscope	No	Yes	Yes	Yes	No	No	No	No
Electron microscope	No	Yes	Yes	Yes	Qualitative	Qualitative	Qualitative	Qualitative
X-ray low-angle scattering	Yes	No	No	No	Sometimes ^b	Sometimes ^b	Yes	Yes
X-ray line width	No	No	No	No	Yes	No	No	No

^aThe term "particle" is used to indicate the separate individual grains of a porous solid; it will therefore include undispersed crystallites. Crystallites refer to the tiny crystals of which the particles may be composed. "Amorphous blocks" is a term used to describe the blocks of which amorphous particles are composed. For example, silica-alumina cracking catalysts are believed to consist of "amorphous blocks" 100 Å on a side, or in diameter.

^bIf the crystallites are sufficiently separated from each other to permit easy access of an adsorbate gas, the "sometimes" becomes a "yes."

in its modified and computationally very cumbersome form with an additional parameter n . For such cases, another well-known technique known as "point B method" can be used. This assumes simply that the beginning of the linear portion of an S-shaped isotherm represents the monolayer saturation volume.

Adsorption and desorption on a surface are determined, in addition to the pressure, by curvature of the capillary. Very often, access to a large pore is through a narrower pore. So while it fills at the large pore dimensions, desorption takes place from the meniscus of the narrow neck. Thus desorption will be delayed with respect to pressure and the adsorption isotherm will not be retraced. This is the well-known hysteresis effect. With assumed models for pore shapes, hysteresis curves can be used to determine pore size distributions.

Chemisorption

Since all the available area is not active in catalysis, chemisorption of specific gases can give more meaningful information, such as an estimate of the time required for contaminants in reactants to poison the catalyst, or area occupied by metals on inactive supports. Examples of such studies on iron catalysts for ammonia synthesis, chromia-alumina in the petroleum industry, and silica-alumina cracking catalysts, have been cited by Thomas [7].

Sedimentation

The rate of settling of particles in a viscous liquid is used to determine particle size (greater than 1000 \AA) using Stokes' law. A deflocculating agent, such as an alkali, is added to prevent agglomeration in the sedimentation method [23].

Electron Microscope

Particles as small as 50 \AA in size may be identified by this technique. The requirements are that the solid be stable under high vacuum and electron bombardment. The main drawback of this technique is that the electron microscope concentrates on a very minute area of about a few millionths of a square millimeter and the values obtained may not be very representative.

X-Ray Methods

Low-angle scattering gives information on the size distribution of tiny crystallites or blocks of amorphous materials. A brief description on X-ray methods is given later.

Mercury Porosimeter

The pressure required to force a nonwetting liquid such as mercury into a catalyst depends on the radius of the pores and the surface tension of the liquid

[45]. By observing the level drop in the mercury reservoir as a function of the pressure, the pore size distribution can be estimated. However, as narrower pores require larger pressures and the commonly available porosimeters have a maximum pressure limitation of 10,000 lb/in.², the smallest radius that can be measured would be about 100 Å. This method is mostly used for macropores of 100 to 45,000 Å. Modern instruments can apply pressures of 50,000 lb/in.² and can measure up to 20 Å.

Densitometers

The pore volume of a solid can be calculated by a simple formula if its pellet density and true density are known. Densitometers measure pellet density by displacement of a nonpenetrating liquid and true density by displacement of helium which fills the pores.

Permeability

The pressure drop in a fluid when it flows at a known rate through a packed bed of finely divided solids gives information on the porosity of the bed.

Other Methods

Harkins and Jura [4] have used heats of wetting on TiO₂ by immersion in water to measure its surface area. Chemisorption or exchange of radioactivity labeled species from vapor or liquid phases may be used to determine active catalyst surface area. As an example, ¹⁴CO adsorption has been used for studying Fischer-Tropsch synthesis catalysts by many investigators. See Refs. 7 and 40.

Methods for Investigation of the Adsorbed Layer

This section focuses attention on the principles involved in the most common methods used for studying the nature of the adsorbed layer on a surface. There has been an explosion in the number of techniques developed for surface studies since the advent of ultrahigh vacuum techniques. The literature is enormous and there are excellent review articles. Information on developments over the years can be obtained from "Analytical Chemistry Annual Reviews."

Thermal Accommodation Coefficient

A gas at a temperature T_1 colliding on a solid surface at a temperature T_2 may adsorb or rebound at a temperature T'_2 . The accommodation coefficient [10] is

defined as

$$a = (T_2' - T_1)/(T_2 - T_1)$$

In general, it can have any value between 0 and 1. It depends on the surface roughness and the presence and nature of adsorbed impurities. As an example, the accommodation coefficient for neon on a clean tungsten wire was 0.06, but it increased to 0.3 when a hydrogen monolayer was present [46]. The presence of a monolayer of any gas, in general, can be verified by this method.

Heat of Adsorption

The heats of adsorption of gases on solid surfaces can be measured by calorimetric methods, but the thermal resistance of catalyst materials and the difficulty in maintaining a constant pressure during adsorption introduce errors in this measurement. Another common technique is to plot adsorption isotherms at two different temperatures and to employ the integrated form of the Classius-Clapeyron equation [10]:

$$\ln \left(\frac{p_2}{p_1} \right)_\theta = \frac{\lambda}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where p_1 and p_2 are the pressures corresponding to the temperatures T_1 and T_2 , respectively, at a constant coverage of θ , and λ is the isosteric heat of adsorption. Variation in λ with coverage or, in other words, the effective surface heterogeneity, can be studied by this method.

Flash Desorption

This method consists in observing the amount of desorbed gas as a function of the temperature. If a sophisticated mass spectrometer is available, study of the nature of the desorbed products and isotopic mixing in the adsorbed layer is possible [46]. If the temperature is increased in a "flash," all the adsorbed gases desorb indiscriminately. This is probably the best method for determining absolute surface areas [47]. When a surface is heated slowly, desorption takes place in discrete steps at specific temperatures. CO shows several weak adsorption states on tungsten and one strong chemisorption state with a carbonyl-type bonding; hydrogen shows molecular and atomic adsorption states on tungsten [28]. Nitrogen shows two different molecular adsorption and one atomic adsorption state on tungsten [32].

Isotopic Techniques

The use of radioactively labeled gases and elements gives information on adsorption energy heterogeneity and poisoning mechanisms. In an often

quoted study, Emmett et al. [48] adsorbed ^{14}CO on an iron catalyst at -78°C and let half the amount desorb at -30°C so that the remaining half could migrate to the more active sites. Followed by adsorption of ^{12}CO at -195°C , ^{14}CO emerged much slower than ^{12}CO when the catalyst was heated, suggesting energy heterogeneity of the adsorption sites. Thomas et al. [7] describe two studies: (1) poisoning of NiO catalysts in the hydrogenation of cyclopropane by ^{203}Hg , hindering hydrogen adsorption, and (2) the exchange of stable isotopes such as deuterium and $^{18}\text{O}_2$ between chemisorbed species and others taking part in a reaction. Exchange of deuterium with paraffins takes place at one or more preferred points and at different temperatures. This can be very informative in heterogeneous reaction studies. Decomposition of nitrous oxide and oxidation of CO on metal oxides have been better understood through exchange studies with $^{18}\text{O}_2$. Isotopic techniques require the use of mass and IR spectroscopy.

Electron Diffraction and Spectroscopy

The development of ultrahigh vacuum equipment made possible the application, to adsorbed layer study, of a number of techniques used for investigating the structure of solids. It became known that, even at pressures as low as 10^{-9} torr, surfaces get contaminated in a few minutes. Ultrahigh vacuum devices can now develop and maintain pressures as low as 10^{-14} torr. The interference caused by adsorbed gases can itself be used for determining the nature and the extent of adsorption. The techniques commonly used are LEED (low energy electron diffraction), CELS (characteristic energy loss spectroscopy), AES (Auger electron spectroscopy), Auger neutralization, and ESCA (electron spectroscopy for chemical analysis). These may be grouped according to the nature of the source for excitation.

Electron Beam as the Source. When electrons hit a target, they produce three different effects [35].

1. Elastic scattering (LEED). If the wavelength of the incident beam is of the same order as the interatomic distances in the solid, diffraction patterns can be observed on a fluorescent screen as dots of varying intensity. As the incident electrons are of low energy (< 500 eV), scattering occurs only from the surface atoms. Adsorption of a gas with a two-dimensionally symmetric structure is different from that of the surface, and changes the diffraction pattern [46]. The major problem with this technique is that the adsorbed layer can produce a diffraction pattern of its own, though of a different intensity.
2. Inelastic scattering (CELS). Some primary electrons suffer characteristic losses, depending on the nature of the surface, and appear at fixed energy differences from the elastic peak. These may be involved in ionizing the surface atoms. CELS involves observing the inelastically scattered electrons.

3. Secondary electron emission (AES). If the energy of the incident electron is sufficient to ionize a surface specie by knocking off an inner shell (K, L) electron, an outer shell electron will try to fill this vacancy. In doing so, it may emit an X-ray or transfer its energy to another electron in its own or a higher orbit, thus exciting it out of the atom. The energy of this secondary electron is characteristic of the parent atom and independent of the energy of the incident electron. The energy distribution of the secondary (Auger) electrons is sensitive to the presence of adsorbed layers. AES is especially good for qualitative identification of light elements.

Electromagnetic Radiation as the Source. AES. Emission of Auger electrons depends upon removal of an inner shell electron, as mentioned above. This may be done in two other ways:

1. X-rays.
2. Ionized rare gases (Auger neutralization). The ionized rare gas may be neutralized by an inner shell electron from the surface atom.

ESCA or XPS (X-ray Photoelectron Spectroscopy). The primary inner shell electron (1s, 2s, 2p) ejected by an X-ray has a kinetic energy which is the difference between the known incident energy of the X-ray and the desired binding energy of the atom. The kinetic energy is determined by deflecting the electron in a magnetic field and observing its path. The calculated binding energy ($E_B = E_I - E_K$) gives only qualitative information. ESCA can be used to identify different oxidation states of metals [28].

Infrared, Visible, and Ultraviolet Spectroscopy

Molecules absorb IR radiation by transitions in bond-stretching and bond-bending vibrations, causing a change in the dipole moment, and visible and UV radiation by transitions of valence electrons. The range of the electromagnetic spectrum typically used is 4000 to 250 cm^{-1} in IR studies and 200 to 750 nm in UV and visible spectroscopy. IR spectra give information on specific bond types such as CH, carbonyl, hydroxyl, carbonates, and sulfates. The observed IR spectrum is a fingerprint for the adsorbed specie, sensitive to structural and chemical modifications at a surface [49]. Unsaturated compounds absorb UV radiation, and long conjugated double bonds absorb visible light. Electromagnetic radiation absorption techniques are probably the most direct method for ascertaining surface complexes. The presence of an adsorption band different from that of the free molecule is a certain indication of chemisorption, though the opposite is not true. Also, physically adsorbed species do not show any shift in their absorption bands. IR spectroscopy has been used mainly for simple compounds such as CO or NH_3 , whereas UV spectroscopy has been employed in heterogeneous catalytic studies of more complicated compounds [7].

Raman Spectroscopy

The information from Raman spectra can often supplement those from the IR spectra. Raman spectra differ from the IR spectra in that the fraction of the incident energy absorbed is very small in the former and also that it involves vibrations that cause a change in the polarizability of the molecule. Polarizability is the ability of a molecule to be deformed in an electric field, separating its charge centers [50]. The IR and Raman spectra of a given compound look very different and they entail radiation of different frequencies, though both involve molecular vibrations. Raman spectra are obtained by using far-UV sources.

Raman spectra are plotted as the intensity of scattering versus the shift in the frequency of the scattered light from the incident [49]. Stokes' lines, which have a longer wavelength than the incident due to energy loss to the sample, are more common than anti-Stokes' lines which are produced by an energy gain from the sample. These lines are usually very weak against the strong background and so a highly monochromatic source is needed. Thus the invention of the laser has given a new impetus to the development of Raman spectroscopy.

Electrical Conductivity

Changes in electrical conductivity occur when a gas adsorbs on a metal, such as hydrogen on nickel [51]. Conductivity of the metal film increases if the adsorbate donates electrons to the conduction band of the metal and decreases if the metal loses electrons to the adsorbate. Thomas et al. [7] mention that measurement of extremely low conductances (10^{-15} to 10^{-10} mho cm^{-1}) has enabled identification of CH_3OH_2^+ and CH_3O^- ions by autoprotolysis of adjacent methanol molecules, when adsorbed on porous silica catalysts.

Work Function and Surface Potential

The energy required to remove an electron from the highest occupied level in a solid is defined as the work function [24]. It can be measured in volts with LEED equipment using the "stopping potential" method [47]. Alternatively, FEM or FIM can be used (see the next section). Adsorption of charged species changes the work function, e.g., when an anionic layer is formed, the barrier for electron removal is higher. The change in the potential difference between the metal and space surrounding it is directly proportional to the dipole moment of adsorption and is termed surface potential [46]. Thus work function measurements give information on surface charge.

Field Emission and Field Ion Microscopy

The instruments for these techniques were developed by Müller. Field emission microscopy (FEM) is capable of higher resolutions (15 to 20 Å) than field

ion microscopy (FIM), but the principles of operation of the two are similar [46]. A thin cold metal wire with a rounded tip of very small radius (10^{-5} to 10^{-4} cm) is placed in a high vacuum surrounded by a spherical glass envelope, coated with a fluorescent material. Voltage of the order of 10,000 V is applied between the tip and the envelope [51]. The large ratio of the radii of the two electrodes produces a field of 10^8 V/cm at the tip [7]. If the tip is negatively charged (as in FEM), this is sufficient for the electrons from the Fermi level of the metal to escape and accelerate toward the screen. Thus an image of the tip is formed on the screen. Magnification is of the order of a million and the intensity of each image point is proportional to the emission current from the corresponding point on the metal. Comparison of surfaces before and after adsorption of gases enables one to "see" adsorption sites and also to calculate the surface potential. Alternatively, if a little helium is introduced into the instrument and the tip is positively charged (as in FIM), helium gets ionized by loss of electrons to the tip and the ions form an image on the screen. FIM has not been developed to the same extent as FEM, which provides information on work function and surface migration of adsorbed species.

Magnetic Susceptibility

The force acting on a sample of mass m and susceptibility, χ , placed in a magnetic field of strength H and gradient $\partial H/\partial x$ is given by the expression

$$f = \chi m H \frac{\partial H}{\partial x}$$

where x is the direction in which the sample is free to move [4]. The instrument commonly used for this measurement is the Gouy balance. This method is restricted to paramagnetic gases which show a change in susceptibility after adsorption. Oxygen, which is a paramagnetic gas, turns diamagnetic when adsorbed on graphite [51].

Electron Paramagnetic or Spin Resonance (EPR, ESR)

When placed in an external magnetic field, electrons in atomic or molecular orbitals align themselves in two discrete orientations with their magnetic moment vectors at an angle of $35^\circ 15'$ along or opposed to the direction of the applied field vector. The energy difference between these two states, known as the Zeeman levels, is given by $\Delta E = g\mu_B H$, where g is the Lande-factor or splitting factor, μ_B is the Bohr magneton, and H is the applied field strength. Microwave quanta with the same energy ($h\nu = g\mu_B H$) can induce transitions between the two states and hence observable resonance. When electrons are paired, their spins are opposed according to Pauli's exclusion principle. Transition of one electron resulting in two parallel spins does not occur. Thus only species with unpaired electrons can be studied and hence the name EPR. It is also called ESR because 99% of the magnetic moment arises out of the

electron spin with a negligible contribution due to the orbital angular momentum.

EPR instruments measure absorption of microwave radiation which is set at a desired incident energy level. A typical scan varies the magnetic field and plots the derivative of the energy absorbed (instead of the energy absorbed) for reasons of electronic convenience. EPR is a powerful tool for studying paramagnetic species on solids such as adsorbed molecules or ions and surface defects such as F-centers and dislocations [52, 53].

Ion and Electron Bombardment

Ion bombardment ejects secondary ions from a metal surface covered with adsorbed gases, and similarly electron bombardment knocks off charged or neutral particles from the surface. Analysis of these ions and particles can give information on the nature of the adsorbed layer. Robertson mentions studies on dissociative adsorption of NH_3 as NH on platinum when two adjacent NH particles recombine to give N_2 and H_2 [46].

Methods for the Study of Solids

The previous section dealt with physical methods used in the study of the adsorbed layer on catalysts. We should mention here that many of these techniques were originally developed for the study of solids. Thus LEED, FEM, and FIM give information on the crystal structure, and AES and ESCA give qualitative information about the surfaces such as the oxidation state. IR and ESR have been used extensively in the study of the structure of zeolites. However, there are other important physical methods that were not discussed in the previous section because they are not applicable to adsorption studies. These are described here.

X-Ray Methods

Diffraction. This is a bulk technique for identifying highly crystalline substances. Diffraction occurs due to the reinforcement of coherent X-rays, elastically scattered by two adjacent atoms, when the difference between the distances traveled by the emerging rays is an integral multiple of the wavelength of the incident X-ray. See Fig. 5. This is mathematically expressed by Bragg's law as $n\lambda = 2d \sin \theta$, where d is the distance between the two atoms, λ is the wavelength of the X-ray, and $(90 - \theta)$ is the angle of incidence. Reinforcement can occur at a number of θ values for a given λ . An X-ray diffraction spectrometer uses a goniometer with a monochromatic X-ray source. Diffraction peaks are observed as a function of 2θ by rotating the sample with respect to the source and the detector at twice the angular speed. The interatomic distances in compounds are determined by the nature of the chemical bonds and so no two substances produce identical spectra. Thus compounds such as metal oxides can be identified by this technique.

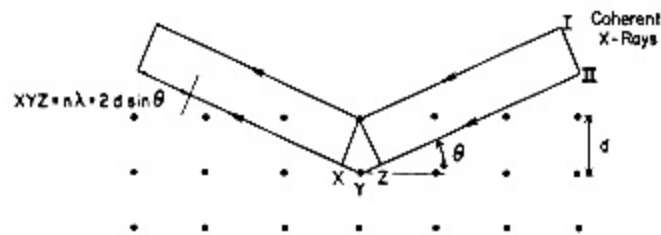


Fig. 5.

X-ray diffraction by surface atoms of a crystalline solid.

Distortions in interatomic distances near solid surfaces will give rise to a phenomenon known as X-ray line broadening. This can be used to calculate curvature at a surface or particle sizes.

X-Ray Fluorescence. X-rays are radiations of high energy capable of ionizing atoms by knocking off inner shell electrons in atoms. If a K electron is knocked off and an L electron fills this vacancy, the energy of the L electron may be emitted as a secondary K_{α} X-ray. If an M electron fills this vacancy, the emitted radiation is a K_{β} X-ray. The energy of the K_{α} , K_{β} X-rays do not depend on the valence state of the atom as the inner energy levels are well shielded in heavy elements.

X-ray fluorescence can be used for quantitative identification of elements heavier than calcium (atomic no. 20) by studying their fluorescent emission under excitation with a continuous X-ray source [50]. The instrument is very similar to that used for diffraction. A counter is used to determine the intensity of the emitted X-rays at various 2θ angles corresponding to different elements that may be in a sample. Quantitative analysis is possible by comparison with a standard of similar composition.

Mössbauer Spectroscopy [54, 55]

A free nucleus emitting a γ -ray suffers a recoil following the laws of conservation of momentum and energy. In a solid, a high-energy γ -ray emission ($E > 1$ MeV) can break loose the nucleus by recoil from its chemical bonds. Less energetic γ -ray emission (150 keV to 1 MeV) can cause lattice vibrations. These two events are not of interest in Mössbauer spectroscopy. Below 150 keV, the entire energy of the nucleus can go into the γ -ray without lattice excitation. Only recoil-free absorption and emission are employed in Mössbauer spectroscopy.

To identify an element, one needs to find an isotope of the same element that can emit a γ -ray without being scattered in the source itself. ^{57}Fe and ^{119}Sn have been two of the most commonly used isotopes. γ -Ray emission and absorption occur at very discrete energy levels like other quantum radiation phenomena. The nuclear levels of an atom are sensitive to its electronic environment. Subtle variations in the source energy are required and are

produced due to the well-known Doppler shift by moving the source at a few mm/s with respect to the absorber. The adsorption bands are plotted as a function of the relative velocity.

Mössbauer spectroscopy can be used for identification of extremely small concentrations of elements (ppb), study of magnetic properties, chemical bonding, and oxidation state of metals. This method has been used extensively for iron compounds [55].

Kinetics

Reactions occurring at the surface of a catalyst proceed through a series of steps. Physical processes of diffusion of the reacting species in and out of the catalyst pores are not usually included in the kinetic treatment. Unlike adsorption and chemical reactions, diffusion is not an activated process. Diffusion in gases shows a temperature dependence to the 1.75 power [56], whereas chemisorption and chemical reaction rates vary exponentially (ex) with temperature. Diffusion is more important in liquid reactions. The ratio of the reaction rate under the influence of diffusion to the theoretical rate is known as the effectiveness factor and can be calculated from a knowledge of the physical properties of the catalyst as described earlier. Thus, only chemisorption, reaction at the surface, and desorption of products need to be taken into account for calculating rates. The usual method is to assume a reaction mechanism and derive a rate expression. While agreement between observed rates and the calculated rates does not necessarily establish the validity of the assumed mechanism, disagreement does indicate that it is incorrect. Kinetics is important in mechanistic studies from the point of view of a chemist and in design calculations from the point of view of an engineer.

The Langmuir-Hinshelwood treatment consists in assuming that the rate of a bimolecular reaction is controlled by the reaction between the adsorbed molecules while reactants and products are in adsorption-desorption equilibrium with the catalyst. A rate expression can be derived as follows:



where K's are equilibrium constants; p's the partial pressures; A(ads), B(ads), and C(ads) the fractions of sites occupied by A, B, and C; and F is the fraction of sites not occupied.

If the surface reaction is rate controlling,

$$r = k_1 A(\text{ads})B(\text{ads})$$

But

$$A(\text{ads}) + B(\text{ads}) + C(\text{ads}) + F = 1$$

or

$$F(K_A p_A + K_B p_B + K_C p_C + 1) = 1$$

Therefore

$$F = \frac{1}{1 + K_A p_A + K_B p_B + K_C p_C}$$

and

$$r = \frac{k_1 K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B + K_C p_C)^2}$$

Similar expressions can be derived if one assumes any of the following steps to be rate controlling:

1. A reversible surface reaction
2. Adsorption of one of the reactants
3. Desorption of the products

and when dissociation of one or more of the reactants takes place, or energetically different adsorption sites are present.

The Eley-Rideal mechanism is fundamentally different from that of Langmuir-Hinshelwood in that it states that only one of the reactants needs to be in the chemisorbed state and the other can react with it from a weakly adsorbed or gaseous state. Rate expressions for these can be similarly derived. For more details, see Refs. 4, 7, and 5759. It is often cumbersome to evaluate all the constants in the rate expressions. Quite often some K_p terms in the denominator of a rate expression (known as the inhibition term) are negligible compared to 1, and the resulting equation may be in terms of the partial pressures of the gases alone. A good example is the hydrogenation of ethylene over Group VIII metals. The rate may be expressed as

$$r = k p_{H_2}^x \cdot p_{C_2H_4}^y$$

the initial orders x and y are about 1 and 0, respectively [7], indicating ethylene is more readily adsorbed than H_2 . Weller has criticized the Langmuir-Hinshelwood treatment. See the section entitled "Rate Expressions."

Absolute Rates of Surface Reactions:
Eyring's Theory

Modern theory of absolute reaction rates as developed by Eyring et al. [60] takes root from the classical Arrhenius rate expression which can be written as $k = A e^{-E/RT}$, where k is the specific rate at a temperature T , and A and E are constants. The significance of the quantities A and E is now evident, though

the original expression written as a logarithmic rate provides no basis for ascertaining their values. The constant A, commonly known as the "frequency factor," is related to the number of collisions in unit volume in unit time, and $e^{-E/RT}$ is the Boltzmann expression for the fraction of molecules having the essential activation energy E above the average level. Most chemical reactions and some physical processes show such temperature dependence. The development of the kinetic theory of gases made it possible to calculate the frequency of collisions in gases as a function of molecular dimensions, masses, and the temperature. The activation energy could be calculated experimentally by linear plots of $\ln k$ vs $1/T$. It was soon realized that not all collisions with the required amount of activation energy result in product formation. The collision theory circumvented this problem by introducing a probability or steric factor P, so that the specific rate $k = PZe^{-E/RT}$. Z represents the number of collisions in a unit volume in unit time. If a reaction is reversible with forward and reverse rates of k_1 and k_2 , the equilibrium constant K may be written as

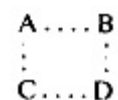
$$K = \frac{k_1}{k_2} = \frac{P_1 Z_1}{P_2 Z_2} e^{-(E_1 - E_2)/RT}$$

$E_1 - E_2$ is clearly the heat of the reaction ΔH , so that

$$K = \frac{P_1 Z_1}{P_2 Z_2} e^{-\Delta H/RT}$$

Since by definition the equilibrium constant $K = e^{-\Delta G^\circ/RT}$, where ΔG° is the standard free energy of formation, $P_1 Z_1 / P_2 Z_2$ should represent the contribution due to an entropy change in the reaction. Eyring et al. [60] consider the free energy of activation and not the heat of activation as the factor determining the specific rate of a reaction.

The underlying assumption of the absolute reaction rate theory is the formation of an activated complex which is in statistical equilibrium with the reactants. The configuration of atoms in the complex can be worked out from a knowledge of its potential energy surfaces which can be constructed by theoretical calculations for simple systems or spectroscopic measurements for complex systems. A reaction proceeds through a series of potential energy minima, and the highest among these represents the state of the activated complex. Thus, as Eyring points out, in a three-atom system, such as a hydrogen atom reacting with a hydrogen molecule in ortho-para conversion, the H-atom approaches the molecule along its linear axis. The activated complex is H . . . H . . . H and now the central H-atom can combine with any one of the two end atoms. When two diatomic molecules AB and CD react involving only the s-electrons, the complex has a planar configuration



where the sum of the distances AD and BC is a minimum before the compounds AC and BD are formed.

Catalytic reactions proceed by formation of adsorbed intermediates on the catalysts, and so the applicability of the absolute reaction rate theory for surface reactions is a logical consequence. Eyring developed expressions for adsorption and desorption on homogeneous and heterogeneous surfaces, mobile and immobile layers, effects of surface interactions, unimolecular and bimolecular reactions, retardation by poisons, dissociative adsorption, and so on. The limitation of space precludes a detailed treatment of these here. We will just mention the molecular adsorption and desorption rate expressions as follows:

$$v_1 = c_g c_s \frac{kT}{h} \frac{f_{\pm}}{F_g f_s} e^{-\epsilon_1/kT}$$

$$v_2 = c_a \frac{kT}{h} \frac{f_{\pm}}{f_a} e^{-\epsilon_2/kT}$$

where v_1 and v_2 are specific adsorption and desorption rates; C_g and C_a are the concentrations of the adsorbed specie in the gas phase and the adsorbed state; C_s is the total concentration of bare sites; ϵ_1 and ϵ_2 are the activation energies of adsorption and desorption per molecule at absolute zero; f_{\pm} , f_a , and F_g , known as the partition functions, are a measure of the probability of occurrence of a molecule in the particular state (\pm activated complex, a adsorbed, g gaseous); f_s is the partition function of the solid adsorption sites; k is Boltzmann's constant; h is Planck's constant; and T is the absolute temperature.

In general, the rate of a reaction is given by the product of the concentration of the complexes at the top of the barrier and the frequency of crossing the barrier to form products. A unique feature of this treatment is the emergence of the factor kT/h , which is a "universal frequency" of crossing the barrier by the activated complex, independent of the nature of the reactants or reactions.

Rate Expressions

This section includes rate expressions for a few important catalytic reactions. Some of these were derived assuming reaction mechanisms and considering adsorption, surface reaction, or desorption to be rate limiting. An excellent article describing this method has been written by Hougen and Watson [59]. Sample calculations with surface reaction as the rate-controlling step are shown in an earlier section for the "Langmuir-Hinshelwood" mechanism. Weller [61] has criticized this approach and points out that simple expressions based on power dependencies with integral and half-integral values are sufficient for most engineering purposes. A summary of his criticism is included.

The rate expressions appearing in this section have been modified from the

original in order to make the notation simpler:

r reaction rate

p partial pressure

K_p equilibrium constant

k specific rate constant

ΔE activation energy

T temperature

θ fractional surface coverage

f fugacity coefficient

and all others unless specified are constants.

Fischer-Tropsch Synthesis on Iron Catalysts [62]

$$r = p_{H_2} \theta_M = \frac{k p_{H_2}}{1 + a p_{H_2O} / p_{CO}}$$

where θ_M is the fraction of the reduced iron in the active zone near the external surface.

Methanol Synthesis

Pasquon et al. derived a rate expression for a trimolecular surface reaction between adsorbed CO and $2H_2$ giving methanol on ZnO-CuO-Cr₂O₃ catalysts (see Ref. 63). The reaction rate can be expressed as

$$r = \frac{f_{CO} p_{CO} f_{H_2}^2 p_{H_2}^2 - f_{CH_3OH} p_{CH_3OH} / K_p}{[A + B f_{CO} p_{CO} + C f_{H_2} p_{H_2} + D f_{CH_3OH} p_{CH_3OH}]^3}$$

Fugacity coefficients have been introduced since under the pressures used in methanol synthesis (300 atm), gases do not show ideal behavior.

Adsorption of CO and H₂ show mutual enhancement in the presence of each other. Thus assumptions of a Langmuir-Hinshelwood mechanism are strictly not valid. Also, there is controversy in the literature about the exact nature of the adsorption complex (see Refs. 64-66). Thus Tsuchiya and Shiba [66] propose reaction between the hydrogen gas and the CO complex in any form on a Zn-Cr-Cu-oxide catalyst so that

$$r = k p_{H_2} A_{CO}$$

where A_{CO} is the amount of CO complex adsorbed.

Sulfur Dioxide Oxidation

Cappelli et al. [67] propose the following rate expression for SO₂ oxidation over vanadium catalyst in a temperature range of 420 to 550°C:

$$r = \frac{k_1 p_{O_2} p_{SO_2} \left[1 - \frac{p_{SO_3}}{p_{SO_2} p_{O_2}^{1/2} K_p} \right]}{[1 + k_2 p_{SO_2} + k_3 p_{SO_3}]^2}$$

$$k_1 = \exp (12.16 - 5473/T)$$

$$k_2 = \exp (-9.953 + 8619/T)$$

$$k_3 = \exp (-71.745 + 52596/T)$$

Michailov et al. [68] checked five kinetic equations and found that with a BAV catalyst the best results were obtained with a simple equation

$$r = k(p_{SO_2} p_{O_2} - p_{SO_3}/K_p)$$

Ammonia Synthesis

$$r = k_2 \left[K_p p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2} \right)^\alpha - \left(\frac{p_{NH_3}^2}{p_{H_2}^3} \right)^{1-\alpha} \right]$$

$$k_2 = k_2(0) \exp \left[-\frac{\Delta E_{k_2}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

$$\Delta E_{k_2} \simeq 38.00 \text{ kcal/mol}$$

Temkin found the value of α to be 0.5 [20].

Weller's Criticism

The essence of Weller's criticism is expressed in his own words, "The Langmuir-Hinshelwood approach . . . does not have the theoretical validity commonly attributed to it, and its use leads to unnecessary mathematical complexity." He argues that [61]:

1. It is inconvenient to obtain the integral rate equation from the differential expression as it entails numerous adsorption constants.
2. The Langmuir adsorption isotherm does not account for the interaction between adsorbed species and the decrease in heat of adsorption with coverage.
3. It predicts a decrease in the amount of one adsorbent in the presence of another. Frequently, the opposite behavior is observed, e.g., mutual

enhancement of CO and H₂ adsorption in the presence of each other on Fischer-Tropsch catalysts.

Weller suggests the following expression for a molecular reaction of $A + B \rightleftharpoons C$,

$$r = k(p_A)^m(p_B)^n(p_C)^q$$

The exponents can have zero, integral, and semi-integral values. He tried to fit experimental data on SO₂ oxidation, hydrogenation of codimers, methanation of CO and H₂, and synthesis of ammonia reactions. The percentage deviation was comparable or higher, but the rate expression is still good enough from an engineering standpoint. As an example, the methanation reaction $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ over nickel-kieselguhr catalyst can be adequately described by $r = k p_{CO} p_{H_2}^{1/2}$ instead of the Langmuir-Hinshelwood expression, assuming a reaction between four adsorbed molecules.

Important Catalytic Process

The following section deals with important catalytic processes. Each section is written to familiarize the reader with the process, catalysts used, and the operating conditions. The references given in each section are designed to introduce the reader to the literature in that area.

Catalytic Cracking

Catalytic cracking is by far the most important catalytic process. The primary objective of catalytic cracking is to increase the yield of high octane gasoline from a barrel of crude oil. Feed to the catalytic cracking process is gas oil boiling range (400 to 1050°F) material. The products from a cat cracker are (1) high octane gasoline, (2) middle distillate, and (3) light olefins and paraffins. Thermal cracking was the principal source of gasoline production until Eugene Houdry first introduced commercial catalytic cracking in 1936. The reactor used was the fixed bed type. The catalyst was activated bentonite clay. Flexibility of feed and better quality of product from catalytic cracking made a revolution in petroleum refining technology. Catalyst in the fixed bed lost its activity very fast and had to be regenerated every 10 min or so. This led to the development of processes which circulate the catalyst continuously between the cracker and the regenerator. Today all the commercial processes [69, 70] use either moving or fluid bed.

In the moving bed process the catalyst is lifted pneumatically to the top of the disengager. After disengagement from the lift gas, the catalyst flows to the reactor where it is contacted with oil vapors and finally flows to the kiln where, after regeneration, it passes to the lift gas engager. Liquid feed rates are

between 1.5 to 4 $V_{oil}/h/V_{cat}$, temperature 850 to 950°F, catalyst/oil wt. ratio 3 to 7. In the fluid bed process the catalyst and the oil vapors are mixed and proceed up the riser cracker. The contact time between the oil and the catalyst is 2 to 12s. There are several designs available, but the difference between designs is mainly mechanical in nature.

A typical catalytic unit is shown in Fig. 6 [71]. Feed oil and hot catalyst from the regenerator are mixed and rise in the transfer line reactor where the cracking takes place. The cracking temperature is usually in the range of 890 to 1000°F. In the stripping section the catalyst is stripped with steam to remove any oil adsorbed on the catalyst. The stripped catalyst goes to the regenerator where the coke on the catalyst is burned off at 1150 to 1250°F with controlled amounts of oxygen to avoid sintering of the catalyst. During regeneration, the coke level on the catalyst is reduced to 0.05 to 0.15 wt.% from 0.5 to 0.8 wt.%. Typically, about 5% of the feed goes to coke. Burning the coke from the catalyst surface is considerably slower than cracking. Five to 10 tons of catalyst is circulated to process 1 ton of oil. Catalytic cracking is essentially an atmospheric pressure operation.

Synthetic silica-alumina and clay were the principal catalysts used in cracking until the early 1960s. With the introduction of zeolites (crystalline silica-alumina) in 1962 by Mobil, cat cracking has undergone a major change [72, 73]. Almost all the catalysts used in present-day processes are zeolitebased catalysts having 10 to 15% zeolite in a silica-alumina matrix. The success of the zeolite catalyst is attributed to its activity which is much higher than that of silica-alumina, better selectivity, and higher resistance to metal poisons such as Ni, V, Fe, and Cu which tend to produce more coke and gas at the expense of gasoline. Higher throughputs are possible with this type of catalyst due to its higher reactivity and higher allowable regeneration temperature.

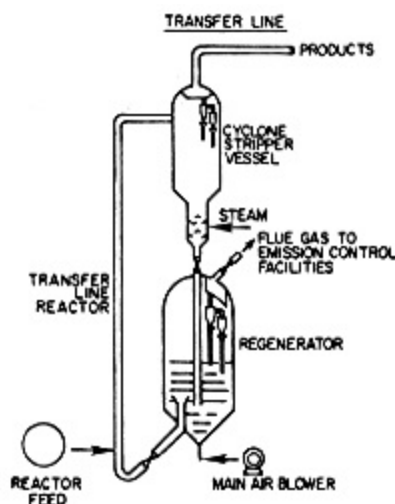
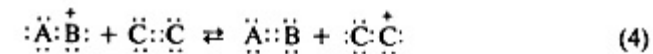
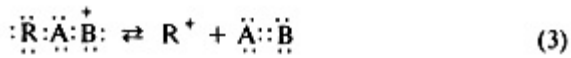
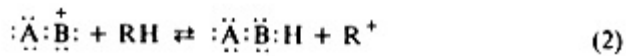


Fig. 6.
Exxon's transfer line cracker.
(Courtesy of Hydrocarbon Processing [71].)

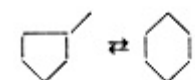
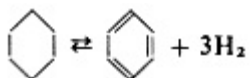
While the carbon deposited on the catalyst can be reduced by burning, metal in the feed accumulates on the catalyst surface. The metal inventory can be controlled by makeup rate or by removal of the metal. Several processes are available for removal of the metal [69]. With feeds containing high levels of impurities like S, N, and metals, hydrotreating is preferred before cracking. This not only lengthens the life of the cracking catalyst but also improves the quality of the feed.

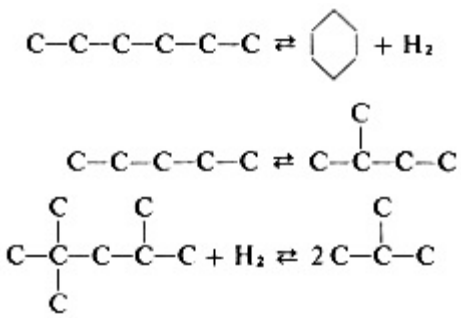
It is generally accepted that the acidic nature of the cracking catalyst is responsible for its activity. While there is agreement about the acidic nature of the catalyst, there is no united opinion as to the nature of the acidic sites on the catalyst. One view is that all acidic sites are Bronsted acid type, another is that it is a Lewis acid, and the third is that it is a mixture of both [39]. Irrespective of the type of acid present, the mechanism of reaction of hydrocarbons is believed to involve carbonium ions. A carbonium ion is deficient by two electrons and it has a positive charge. An excellent review of carbonium ion reactions for each class of hydrocarbons is reported in the literature [38, 74]. The carbonium ion is believed to undergo the following four generalized types of reactions:



Reforming

The primary purpose of reforming is to increase the octane number of naphtha going to the gasoline pool. Of secondary importance is its use in the production of aromatics for petrochemicals. This process is of importance because of present-day needs as well as in a historic sense. During World War II, toluene which was used in the manufacture of TNT was produced by reforming of petroleum fractions rich in methyl cyclohexane using MoO₃ on γ -alumina. It is of importance today because the loss in octane number due to the elimination of lead from gasoline has to be primarily compensated for by the high octane product from the reformer. Important reactions taking place during reforming are





Dehydrogenation of C₆ naphthenes is a fast reaction compared to dehydrocyclization of paraffins, isomerization, and dehydrogenation of cyclopentanes.

UOP announced the first commercial reforming unit using platinum on alumina catalyst in 1949. Relatively long life and very low loading of the expensive platinum (0.3 to 1%) on alumina made this process economically competitive. Another big step forward was made when Chevron announced its bimetallic Pt/Re on alumina reforming catalyst in 1969. These catalysts had even longer life than platinum catalysts. The longer life of these catalysts is attributed to the ability of rhenium to stabilize the finely divided platinum and prevent agglomeration when subjected to severe operating conditions [75]. The use of these bimetallic catalysts in United States refineries has increased from 27% in 1972 to 60% as of January 1977 [76].

Reforming is carried out at pressures of 150 to 500 lb/in.² and temperatures between 450 and 550°C. Thermodynamic considerations favor low pressure and high-temperature operation. Elevated pressure is necessary to maintain the activity of the catalyst for longer periods of time whereas low temperatures are preferred to prevent cracking and the resulting loss in liquid yield from the reformer. The time between regenerations of the catalyst can be increased from a few days to a few months by raising the operating pressure from 150 to 600 lb/in.². With improvements in reforming catalyst, the reformer operating pressure has been going down as shown in Fig. 7 [77]. Acidity of the alumina matrix can be controlled by the introduction of suitable amounts of halides. Arsenic, copper, and lead are permanent poisons for the platinum catalyst. Due to the endothermic nature of the reactions taking place during reforming, it is carried out in three or four stages with heating between stages. Liquid feed rates and the H₂/hydrocarbon mole ratio used vary from 1 to 4 and 2 to 10, respectively. Several review articles on reforming have appeared in the literature [78-80].

Hydrotreating

Hydrotreating is one of the most important processes in a modern refinery. In 1976 the United States hydrotreating capacity was 40% of the crude capacity [81]. This percentage is expected to increase steadily. Hydrotreating is the process by which N, S, O, and metals are removed from petroleum fractions. It

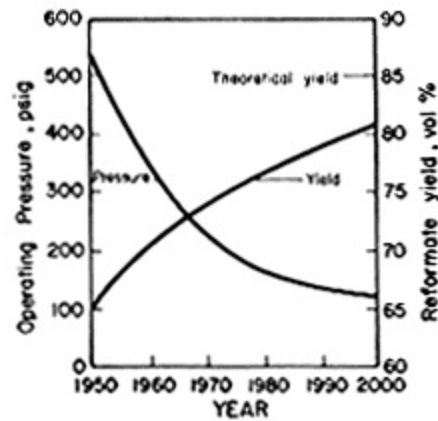
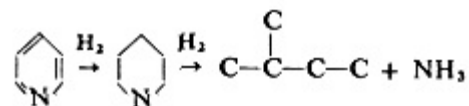
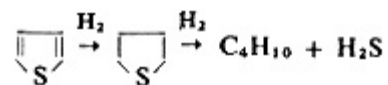
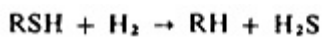


Fig. 7.
Catalytic reforming projections.
(Courtesy of Oil & Gas Journal [77].)

is employed in industry for one of the following reasons: (1) to improve the quality of the downstream product, (2) to protect and improve the performance of catalysts used in downstream operations, (3) to reduce the sulfur content of the fuel to meet environmental restrictions, and (4) occasionally to improve the stability of the product. Availability of inexpensive hydrogen from reformer operation has given a boost to this process. Sulfur, N, O, and metal contents are generally higher in the higher boiling range material. Previously, only light fractions were hydrotreated. Presently, processes have been developed for residues also. Hydrogen consumption depends on the sulfur, nitrogen, and oxygen of the feed and the extent of hydrogenation of feed aromatic content. Hydrogen consumption varies from about 200 scf to 1000 scf/bbl of charge.

It is essential to hydrotreat the feed to the reformer to protect the platinum catalyst from sulfur poisoning. Hydrotreating of the feed also improves the yield and quality of the reformate, lengthens the life of the catalyst, and increases the regeneration cycle time. Hydrotreating the feed to the catalytic cracker lengthens run time, improves the selectivity for cracking, and improves the quality of the product. By decreasing the sulfur content of coke on the cracking catalyst, the amount of sulfur oxides emitted to the atmosphere during regeneration is reduced. Typical reactions taking place in hydrotreaters have been reported in the literature [82]. Some of them are



The most common catalyst used in hydrotreating is CoMo oxides on alumina [83]. Other catalysts, NiMo and NiW on alumina oxides, may also be used. Generally, these catalysts are converted to the sulfide form using some source of hydrogen sulfide before use. Hydrotreating is carried out in fixed bed reactors. Typical operating conditions employed are: temperature, 300 to 400°C; pressure, 20 to 40 atm; LHSV, 1 to 5 $\text{V}_\text{L}\text{V}_\text{c}^{-1} \text{ h}^{-1}$. A hydrogen/hydrocarbon mole ratio as high as 10 is used. The phase of operation may be vapor, liquid, or mixed. Liquid yields of 97 to 98 vol.% can be obtained. As in hydrocracking and reforming operations, loss in activity of the catalyst with time can be compensated for by increasing the hydrotreater operating temperature. A collection of patent literature on hydrodesulfurization from 197075 is available [84].

Hydrocracking

Hydrocracking was used in Germany as early as 1924 to upgrade the coal-derived liquid from the hydrogenation of brown coal by the Bergius process [99]. The catalysts developed were all the well-known hydrotreating catalysts in use today. Of particular interest was nickel tungsten sulfide. Gasoline produced by this catalyst had poor antiknock qualities because of the high hydrogenation activity of the catalyst. This led Pier to develop a tungsten sulfide on montmorillonite catalyst. Montmorillonite, which has acidic properties, supplied the cracking activity whereas tungsten sulfide gave the hydrogenation activity. All the hydrocracking catalysts used today are basically this dual function type, the variation being in the type of hydrogenation and cracking components used.

Hydrocracking can be employed to process gas oils and more refractory feedstocks such as catalytic cracking cycle stock and products from coking operations which cannot be cracked directly in a catalytic cracker. The products of hydrocracking include gasoline, lubricating oil, catalytic cracking feedstock, steam cracker naphtha, BTX precursors, and LPG [86]. The versatility of this process is demonstrated by its ability to change the product distribution by varying the operating conditions. Since the introduction of the modern version of hydrocracking, it has experienced considerable growth. The future looks even brighter since this process is suited for synthetic crudes from coal, oil shale, and tar sand which are low in H/C ratio when compared to petroleum. A modern hydrocracking process operates around 400 to 900°F and 100 to 3000 lb/in.² gauge. The space velocity is in the range of 0.5 to 10 $\text{V}_\text{L}\text{V}_\text{c}^{-1} \text{ h}^{-1}$. As much as 5 bbl of products can be obtained from 4 bbl of feedstock. Hydrogen consumption varies from 300 to 2000 scf/bbl depending on the severity of operation. Unlike catalytic cracking, hydrocracking is carried out in a fixed bed reactor because of the long life of the catalyst used. The catalyst can be used as long as 3 years before it needs regeneration or replacement. Decrease in the activity of the catalyst can be compensated for by raising the temperature of operation.

Hydrocracking can be carried out in one or two stages [85]. Single-stage processes generally are used to produce middle distillates from heavy vacuum

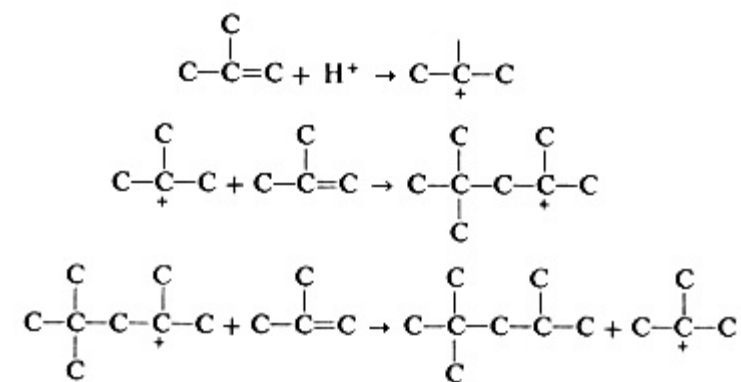
gas oils. Two-stage processes are primarily used to produce gasoline from cracked and virgin gas oil. The first stage of the two-stage process is to hydrotreat the feed to the second stage so that nitrogen impurities which poison the cracking component and sulfur which poisons the hydrogenation components can be reduced. Part of the aromatics are also hydrogenated in the first stage.

Hydrogenation-dehydrogenation activity is supplied by metals such as Ni, Mo, W, V, Pt, Pd, and their oxides and sulfides or a combination of two [86]. Cracking activity is supplied by Y-type zeolites, silica-magnesia, silica-zirconia, silica-titania, and fluorided alumina. The relative strength of hydrogenation and cracking functions can be adjusted to give predominantly hydrogenation or cracking activity. Noble metals are used only in the second stage or with feeds containing low levels of impurity. The long life of the hydrocracking catalyst is attributed to the hydrogenation component which keeps the acid sites clean by hydrogenating the coke precursors. Catalyst requirement for specific needs [85] and the mechanism of reactions taking place during hydrocracking [87] are reported in the literature.

Alkylation

Alkylation is an important way of making high octane components for the gasoline pool. Isobutane is reacted with C₂, C₃, C₄, and C₅ olefins in the presence of catalysts to give alkylate. Most alkylation units combine isobutane with C₃, C₄ and C₅ olefins. As the normal paraffins do not react with olefins (for lack of tertiary hydrogen), they have to be isomerized to branched paraffins before alkylation.

Sulfuric acid and hydrofluoric acid are the most commonly used catalysts. It is essential to keep the concentration of the acid 89 to 98% and the paraffin-olefin ratio high (5/1 to 15/1) to promote the alkylation reaction and to reduce polymerization of the olefin. A simple sequence of reactions is



Olefins dissolve easily in the acid whereas paraffins do not. Intense mixing is essential to bring about contact between the acids, olefins, and paraffins. Therefore, the thrust in alkylation reactor design is to increase the interface

area for mass transfer. Another important parameter to be considered in reactor design is the temperature control [88]. Acid-to-hydrocarbon ratios of 1 to 3 are employed in commercial operations. The contact time for the olefins is around 15 min. After completion of the alkylation reactions the acid is separated from the alkylate in a settler. Hydrogen fluoride is usually recovered by distillation and reused whereas H_2SO_4 is often discarded after one use [69]. Recovery of acid from spent black sulfuric acid is difficult and expensive, consequently use of HF is increasing.

Low temperatures and sufficient pressure to assure a liquid phase are required for alkylation. Sulfuric acid alkylation is carried out around 10°C . Going to lower temperature increases the power consumption for mixing exponentially because of the increased viscosity of the acid. At higher temperatures, formation of unwanted products increases due to the enhanced oxidizing ability of H_2SO_4 . Refrigeration is essential with H_2SO_4 alkylation to remove the heat of reaction (20 kcal/mol). With HF, alkylation is carried out at higher temperatures, 25 to 35°C . This is necessary to compensate for the lower activity of HF. Under these temperatures the oxidizing ability of HF is less than that of H_2SO_4 . The advantage of this process is that cooling water can be used to remove the heat of reaction. Water is a poison in the sense that it dilutes the acid. Butadiene is also a poison as it wastes about 20 kg of acid for every kg dissolved in the acid.

Ethylene is rarely used as alkylation feed because of its higher petrochemical dollar value. Other alkylation processes and catalysts used are discussed elsewhere [75]. The use of molecular sieve zeolite catalysts in alkylation, particularly for ethylene alkylation of benzene, is a promising new process [107].

Isomerization

Isomerization processes are used in the petroleum industry for the production of additional feed for alkylation or to produce high octane components for the gasoline pool from n-paraffins. Isobutane is the most important isomerization product for alkylation. Pentane-hexane isomerization is carried out to produce high octane components for the gasoline pool. The difference in octane number between different isomers is shown in Table 2 [88]. Isomerization is usually restricted to C_4 , C_5 , and C_6 paraffins. Higher paraffins not only tend to crack more and deactivate catalysts, but also their isomers are not easily separable. Lower temperatures favor the formation of branched isomers.

Predominantly, two types of catalysts are used in this process: (1) Friedel-Crafts metal halides and (2) dual functional catalysts, the latter being by far the most important. Aluminum halide catalysts promoted by HCl are difficult to handle and produce tars which require special means for disposal. The use of AlCl_3 for isomerization is obsolete today. Dual functional catalysts having platinum or other noble metals on acidic supports are used today. These catalysts have very high selectivity but need high temperatures for activation. However, thermodynamics favors low temperature operation (Fig. 8). With the development of highly acidic supports, operating temperature has been

TABLE 2 Isomer Properties (courtesy of American Chemical Society [88])

	Boiling Point (°F)	Vapor Pressure (at 100°F)	RON, Clear	MON, Clear	RON, 3 cc TEL	MON, 3 cc TEL
Isobutane	10.9	72.2	102.1	97.0	118.3	
n-Butane	31.1	51.6	94.0	89.1	104.1	104.7
Isopentane	82.1	20.4	92.6	90.3	103.5	106.9
n-Pentane	96.9	15.6	61.7	61.3	84.7	83.6
Cyclopentane	120.7	9.9	101.3	85.0	111.1	95.2
2,2-Dimethylbutane	121.5	9.9	92.3	92.9	103.4	114.6
2,3-Dimethylbutane	136.4	7.4	103.5	94.3	112.0	109.7
2-Methylpentane	140.5	6.8	73.4	72.9	92.2	92.4
3-Methylpentane	145.9	6.1	74.5	74.0	92.3	92.6
n-Hexane	155.7	5.0	34.0	25.0	65.3	63.5
Methylcyclopentane	161.3	4.5	95.0	80.0	104.3	91.1
Cyclohexane	177.3	3.3	83.0	77.2	97.4	87.3

lowered to 200 to 400°F from 820 to 950°F [88]. Typical operating conditions for C₄ isomerization are: temperature, 300 to 400°F; pressure, 200 to 400 lb/in.² gauge; LHSV, 3 to 5 $\text{V}_\text{L} \text{V}_\text{c}^{-1} \text{ h}^{-1}$. For C₅/C₆ isomerization, the operating conditions are: temperature, 250 to 550°F; pressure, 200 to 1000 lb/in.² gauge; LHSV, 1 to 3 $\text{V}_\text{L} \text{V}_\text{c}^{-1} \text{ h}^{-1}$; H₂/hydrocarbon mole ratio, 1 to 4. Water content of more than 100 ppm in the feed has been found to interfere with the function of the catalyst. Catalyst life is of the order of years. The presence of hydrogen has been found to be helpful in suppressing the polymerization of olefins formed during isomerization.

Polymerization

Polymerization has two distinctly different applications. In the petroleum industry this process is used to produce gasoline boiling range materials from C₂, C₃, and C₄ olefins. It is one of the oldest processes in the petroleum industry. The first commercial application of this process started in 1937. The other application of polymerization is for the production of polymers from C₂, C₃, and C₄ olefins. One of the most important catalysts used in polymerization is the Ziegler-Natta type. In 1949 Ziegler and his co-workers at the Max Plank Institute for Coal Research discovered that a combination of metal alkyls of Groups III and transition metal compounds from Groups IV-VIII of the periodic table was an active polymerization catalyst. Before the discovery of this catalyst, polyethylene was made at a pressure of 1000 atm and 500°F. With this catalyst the polymerization can be carried out at room temperature and pressures as low as 10 atm. Natta and his co-workers made an even greater contribution to polymer chemistry by discovering that the Ziegler-type catalyst produced stereospecific polymers. Stereospecificity makes polymers

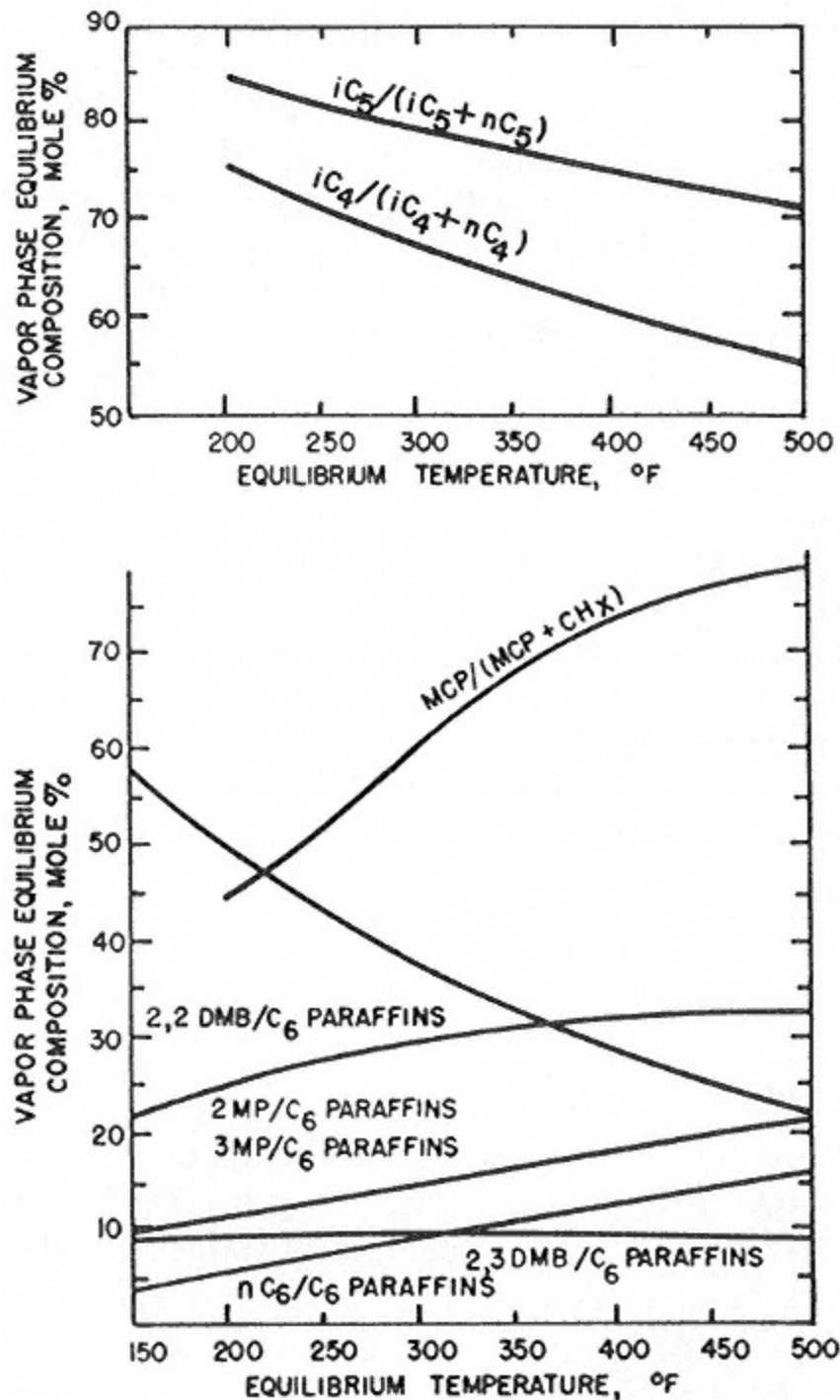


Fig. 8.

Vapor-phase equilibrium composition for butanes, pentanes, and hexanes.
(Courtesy of the American Chemical Society [88].)

more dense, increases the melting point, and makes them stronger and stiffer. For these very important contributions, Ziegler and Natta were awarded the Nobel prize in Chemistry in 1963.

Gasoline produced from olefin polymerization is a high octane material used to increase the octane number of the gasoline pool. For this type of application, the reaction is stopped after dimerization. The catalyst used for this process is phosphoric acid. Depending on the process, solid phosphoric acid on a neutral support or liquid phosphoric acid is used. This reaction is exothermic in nature (25 to 30 kcal/g·mol of dimer).

Temperature control is attained by carrying out the reaction in heat exchanger-type reactors. Polymerization is carried out in a fixed bed reactor, and 350 to 400 ppm of water in the feed is the optimum level needed for proper functioning of the catalyst [75]. Operating conditions are 200 to 220°C and 400 to 1200 lb/in.² gauge. Ammonia, oxygen, and butadiene are poisons for phosphoric acid catalyst.

Institut Français du Pétrole (IFP) claims that its process for the dimerization of propylene has 90% selectivity to dimer with conversions in excess of 95% per pass. The process catalyst which is not disclosed is discarded after one use [89].

Two types of catalysts are used for the polymerization of olefins to high molecular weight materials [70]: the Ziegler-Natta catalyst consisting of combinations of aluminum alkyls $Al(R_3)$ and titanium tetrachloride (wherein a complex between the two components is very important), and the solid supported metallic oxide catalyst. Both catalysts have widespread commercial applications.

Operating conditions for the manufacture of polyethylene using Ziegler-Natta catalysts are in the range of 50 to 75°C and 10 atm. A slightly higher temperature is used for propylene to compensate for its lower reactivity compared to ethylene.

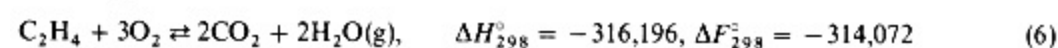
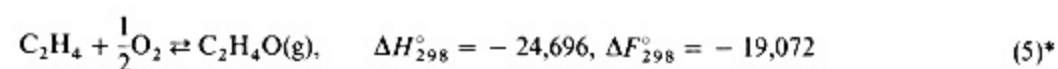
An example of the supported metallic oxide catalysts is that used by AMOCO Chemical Co. for the production of polyethylene. It is reported to have 7 to 25% molybdena on 20/200 mesh γ -alumina [75]. The process operates between 240 and 300°C and 35 to 100 atm. Phillips Petroleum Co.'s process for polyethylene uses 2 to 3% Cr_2O_3 on silica-alumina (90% SiO_2 , 10% Al_2O_3 cracking catalysts). In both processes the catalyst is suspended in a solvent, and olefin is added to the slurry. After completion of the reaction, polymer is separated by filtration, and catalyst and solvent are recycled.

The mechanisms of reaction for both the Ziegler-Natta catalysts and the supported oxide catalysts have been studied extensively. The reader is referred to Ref. 90 for information on this subject.

Ethylene Oxidation

Ethylene oxide is the most important of all the oxides of olefins. It is mainly used as a chemical intermediate. The importance of ethylene oxide is attributed to two of its properties: (1) its ability to combine with chemicals containing replaceable hydrogen, and (2) its capacity to polymerize and give polyethenoxy chains [91]. It was first discovered by Wurtz in 1859. He believed that oxygen could not be added directly to ethylene, so he developed the chlorohydrin process involving the addition of hypochlorous acid to ethylene followed by dehydrochlorination. Nearly 75 years later, Wurtz was proved wrong. In 1931 a patent was issued to Lefort for direct oxidation of ethylene to ethylene oxide using silver catalyst [92]. Today all the ethylene oxide comes from this process.

The two main reactions which take place during the oxidation of ethylene are [93]:



Thermodynamic values indicate that the unwanted strongly exothermic com-

*All ΔH° and ΔF° hereafter are cal/g·mol.

bustion reaction is favored over the partial oxidation of ethylene to ethylene oxide. Selectivity of the catalyst to accelerate the ethylene oxide formation reaction is very essential. Silver catalyst moderated with chlorine has been successfully used in commercial operations.

Several commercial processes are available for the oxidation of ethylene to ethylene oxide. The catalyst used in all these processes is metallic silver on a low surface area inert support. Electronegative moderators have been found to be necessary for improvement in selectivity. Too much moderator, however, destroys the catalyst activity. The moderators which are known to improve selectivity of silver are Cl, Br, I, S, Se, Te, P, and Bi [92]. Chlorine is the most commonly used moderator. About 1 ppm of chlorine in the feed improves the selectivity from 45 to 7075%. Depending on the process, a mixture of ethylene and air or oxygen is passed over a fixed bed catalyst in a heat exchanger type of reactor. Heat transfer is an important factor in reactor design. Operating conditions are in the range of 200 to 300°C and 10 to 30 atm. Reaction time is of the order of a few seconds. Catalyst life of 8 yr without loss in activity and selectivity has been reported. The highly exothermic nature of the reaction led to the study of this reaction in fluidized beds which have better heat transfer characteristics. However, many other disadvantages of the fluid bed reactor prevented extensive application to commercial operation.

Ethylene oxide from the effluent gas is removed by absorbing it in water and later recovering it by flashing. The use of air requires a second stage to react any remaining ethylene. If oxygen is used, the effluent from the first stage is recycled after separating the ethylene oxide.

Improved selectivity when using small amounts of chlorine is attributed to the partial poisoning of the silver sites active for oxygen adsorption. The reaction is believed to involve oxygen adsorbed on the catalyst surface. Two views exist regarding the mechanism of ethylene oxidation. One view is that the reaction takes place between the adsorbed oxygen and adsorbed ethylene, namely the Langmuir-Hinshelwood mechanism [92]. The other is that the reaction takes place between adsorbed oxygen and ethylene from the gas phase, the Rideal mechanism [94].

Steam Reforming of Light Hydrocarbons

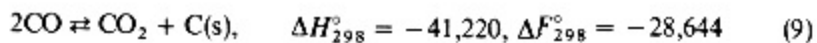
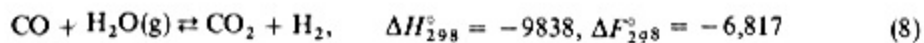
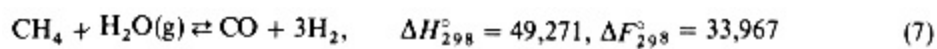
Mixtures of carbon monoxide and hydrogen are generally referred to as synthesis gas. Such mixtures are raw materials for (1) methanol synthesis, (2) the oxo process for the manufacture of primary alcohols and aldehydes, (3) Fischer-Tropsch synthesis, and (4) methanation to make synthetic natural gas (SNG). The processes for making synthesis gas involve catalytic steam reforming of light hydrocarbons, and partial oxidation of heavy hydrocarbons or coal gasification. The discussion here will be restricted to catalytic steam reforming of light hydrocarbons, i.e., CH₄ and naphtha.

Almost all the synthesis gas produced in the United States is from natural gas. On the contrary, nonavailability of natural gas in Europe and Japan has led to the development

of catalytic steam reforming based on naphtha. But

with the changing energy picture, the heavier fractions of crude oil and coal are being looked upon as feedstocks for the production of synthesis gas. A block diagram for synthesis gas production as it applies to ammonia production is shown in Fig. 9.

The stock to the reformer is desulfurized using activated carbon fortified with metallic additives for feeds containing up to 10 ppm of sulfur. For high sulfur feeds a more sophisticated system containing cobalt molybdate backed by iron or zinc oxide to absorb the sulfur is used [95]. Desulfurization of the feed is essential because the nickel catalyst in the reformer is poisoned by sulfur. Desulfurized feed is fed to the reformer. The main reactions taking place in methane reforming are [93]:



The first two reactions (reforming and shift) are desired, whereas the last is undesired as it deactivates the catalyst by forming coke. This also increases the pressure drop in the reformer tubes. As the reforming reaction is endothermic, higher temperature would shift the equilibrium in the desired direction. The stoichiometry of the reforming reaction suggests that lower pressure would be preferred. However, it has been found to be more economical to operate the reformer at higher pressures [96]. With the development of suitable catalysts and materials of construction, the reformer pressure has gone up to 40 atm from 2 to 5 atm. Increased coke formation at high pressure can be reduced by raising the steam/hydrocarbon ratio and the temperature. Single-stage reform-

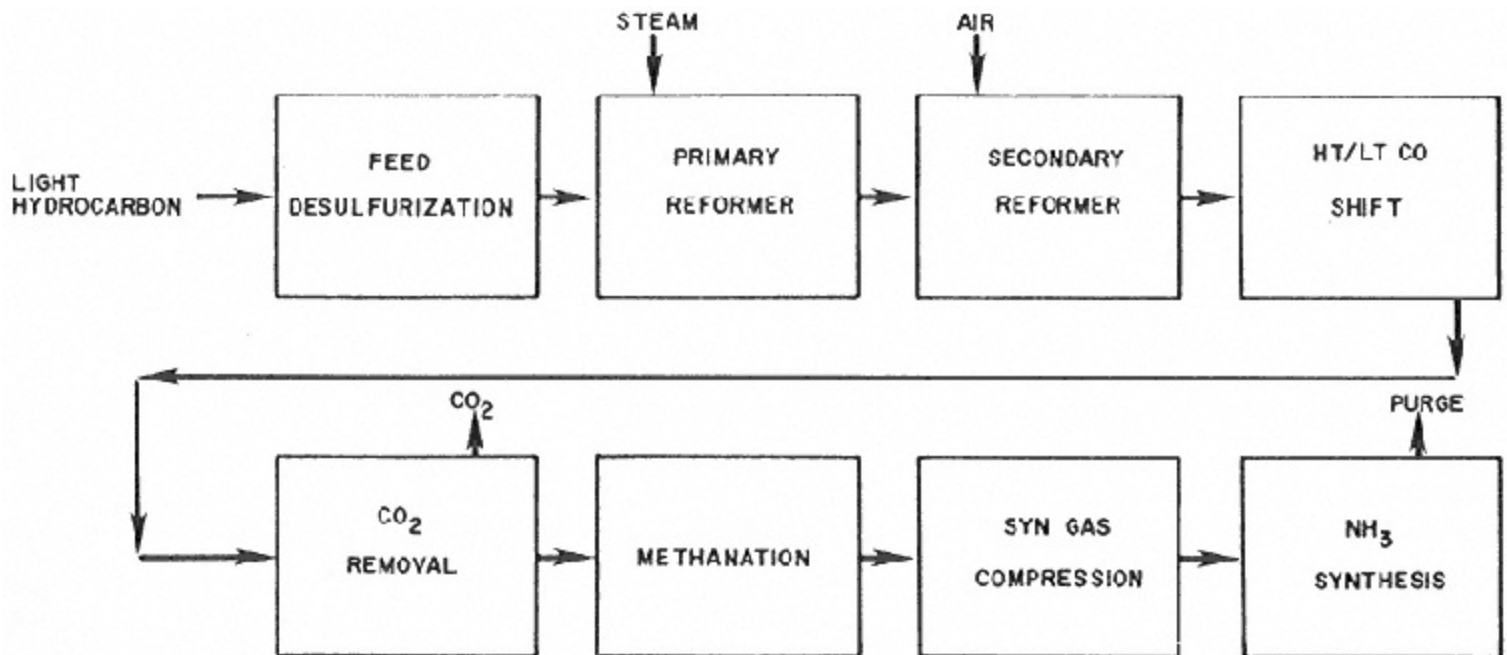


Fig. 9.

Typical ammonia process based on catalytic steam hydrocarbon reforming.

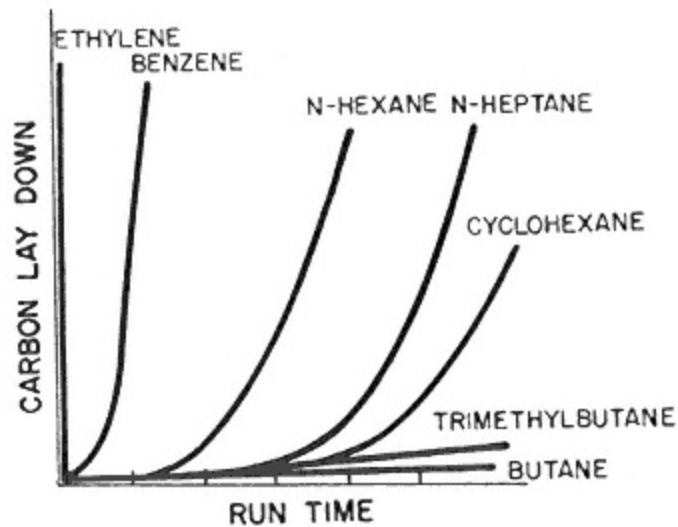


Fig. 10.
Carbon lay down of different hydrocarbons.
(Courtesy of Chemical Engineering Progress [97].)

ing is employed for synthesis gas going to methanol, SNG production, or H₂ production. The catalysts used are 15 to 35% NiO on a ceramic base of calcium and aluminum oxides. With low levels of impurities in the reformer feed, catalysts have been used for as long as 20 yr [93].

Where steam reforming is used as a source of synthesis gas for ammonia production, an additional reforming step is required for methane reduction. Air is injected into the primary reformer gas and the mixture is passed over the catalyst at temperatures in excess of 1000°C. The catalyst is a supported nickel oxide of low silica content.

With decreasing availability of natural gas, interest in the reforming of heavier feedstocks is increasing. However, heavier feeds tend to coke up the catalyst. Figure 10 illustrates the relative deactivation tendency of different compounds [97]. Improved catalysts have been developed for reforming of heavier feeds. These involve alkali addition to the nickel-based catalyst. Alkali promotion (7 to 10% Na₂O or K₂O) has been found to control carbon formation with naphtha-range feedstocks [20].

Shift Conversion

Shift conversion processes are used to remove carbon monoxide from synthesis gas where hydrogen or ammonia is the desired product. The process is also used to adjust the H₂/CO mole ratio of synthesis gas for SNG production and Fischer-Tropsch synthesis.

The conversion reaction is



Shift conversion can be carried out in one or two stages. In the two-stage operation, the first is operated at temperatures between 350 and 425°C while the second is operated at about 250°C. Since the reaction is exothermic, cooling is accomplished between stages. The pressure of operation is generally controlled by the operating pressure of the

preceding synthesis gas preparation

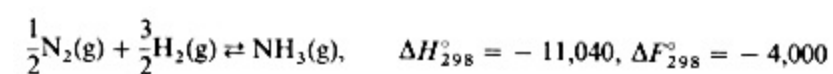
step. The catalyst in the high-temperature stage is iron oxide-chromia and in the low-temperature stage is copper oxide-zinc oxide-alumina. The composition of ICI catalyst 5211 for low-temperature operation is said to be CuO:ZnO:Al₂O₃ in a weight ratio of 30:45:13.

Ammonia Synthesis

With rising world population the demand for nitrogenous fertilizer is on the increase. Nitrogenous fertilizers are produced by the fixation of atmospheric nitrogen in the form of ammonia. The importance of fixation of nitrogen was realized long ago in the time scale of history. However, it was not until 1905 that commercial feasibility of the synthesis of ammonia from N₂ and H₂ was possible. At that time Haber, employing bulk iron as a catalyst, demonstrated that 0.005% of NH₃ was in equilibrium with stoichiometric N₂ and H₂ gas at 1000°C and atmospheric pressure. By 1909 Haber had developed a unit to make 80 g of ammonia per hour with an osmium catalyst. The process was named after the inventor of the process, Haber, and the designer of the pilot-plant equipment, Bosch, of Badische Anilin Soda Fabrick (BASF). A few years later the world's first commercial synthetic ammonia plant went into production at Oppau, Germany [96]. The catalyst used today is basically the same as the one developed by Mittasch at BASF: iron promoted by metallic oxides. Operating conditions were 400 to 650°C and 150 to 1000 atm. Reciprocating compressors were used to compress the synthesis gas. Multiple production trains were used for large capacities.

The introduction of centrifugal compressors by M. W. Kellogg Co. in the 1960s revolutionized ammonia technology. Single train operation with capacities as high as 2000 tons/d became a reality.

The equation for NH₃ synthesis is



As the conversion of nitrogen and hydrogen to ammonia is an exothermic reaction, lower temperature is favorable for high equilibrium yields of ammonia. As it is also accompanied by a reduction in the number of moles, equilibrium is favored in the desired direction with higher pressure. The inertness of nitrogen is demonstrated by its heat of dissociation of 171 kcal/mol as compared to 118 kcal/mol for oxygen and 104 kcal/mol for hydrogen [93]. Several attempts to react atomic hydrogen with molecular nitrogen have failed because of the high dissociation energy of the nitrogen molecule. This makes it necessary to have a catalyst to lower the activation energy. This reaction has been studied extensively because of its industrial importance and because of its simplicity which proceeds without the formation of by-products. There are several commercial catalysts available. They are all basically a magnetite-type of iron oxide promoted with small quantities of potassium, aluminum, calcium, etc., as oxides. The ICI catalyst is stated to have the following components: 0.8% K₂O, 2% CaO, 0.3% MgO, 2.5% Al₂O₃,

0.4% SiO₂, and traces of TiO₂, ZrO₂, and V₂O₅ [20].

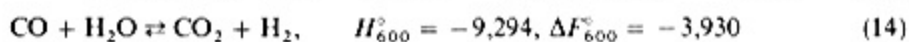
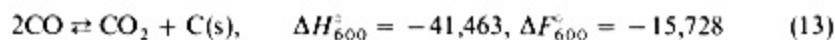
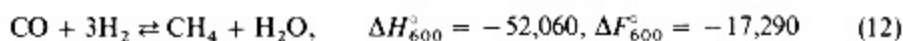
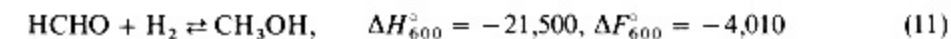
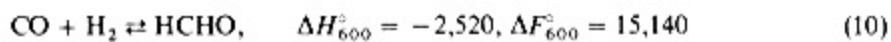
There are several processes available for the synthesis of ammonia. The

main difference between the processes is the pressure employed and the design of the ammonia converter. The large quantities of heat evolved during the reaction is utilized to preheat the feed. Temperature control is achieved by quenching with cold feed at different stages of the converter. Operating conditions for a typical converter are 450 to 520°C, 140 to 300 atm, and LHSV of 10,000 to 55,000 $\text{V}_L \text{V}_c^{-1} \text{h}^{-1}$. Fifty to 80% of the equilibrium value of ammonia is obtained per pass. Ammonia is separated from the exit gases by cooling with water in a heat exchanger. Refrigeration is also employed to recover more ammonia before the gases are sent to the booster compressor which recycles the gases back to the converter. The new Kellogg converter is a horizontal heat exchanger type [95]. Catalyst poisons include CO, CO₂, O₂, and H₂O. Catalyst life of 3 to 5 yr is not unusual. The level of inerts in the feed to the converter can be controlled by purging part of the recycle gas.

Methanol Synthesis

The process of the synthesis of methanol followed the development of ammonia synthesis by the Haber-Bosch process. The high-pressure technology necessary for methanol synthesis was fairly well developed by BASF as described for NH₃. The effect of pressure and thermodynamic considerations are similar for both processes. Before the announcement by BASF of the first commercial process in 1926, methanol was produced by wood distillation. At present essentially all 4 billion lb/yr of methanol produced in this country come from synthesis [91]. The design of the methanol converter is similar to that for ammonia. A large percentage of methanol produced is used to make formaldehyde which is a raw material in the manufacture of synthetic resins. With the decline in petroleum resources, it is also being examined as an automobile fuel either in pure form or as a 10 to 15% mixture with gasoline.

The reactions to consider in methanol synthesis are [93]:



Reactions (12), (13), and (14) are unwanted side reactions. As the free energies indicate, thermodynamically the formation of by-products is favored compared to the synthesis of methanol. Hence it is essential to have a catalyst with high selectivity toward methanol formation. The catalyst used in most methanol converters is zinc oxide promoted with 20 to 25% chromium oxide [75]. Operating conditions are: temperature, 300 to 400°C; pressure, 100 to 600 atm; H₂/CO mole ratio, 2.1 to 2.5. Conversion per pass is kept around 5% to minimize by-product formation. Synthesis gas produced by methane steam-reforming has a H₂:CO mole ratio of 3:1. This ratio is decreased to the desired level by adding CO₂ to the reformer feed. Under the reaction conditions

employed in a methanol synthesis reactor, CO reacts with the walls of the reactor and produces iron carbonyl which deposits on the catalyst and accelerates its deactivation. This and other disadvantages of the high-pressure operation led to the development of the low-pressure process using copper as a component of the catalyst [98]. This process operates at 50 atm and uses tubular heat exchanger-type reactor.

Copper-containing catalysts have been known for a long time for superior activity for methanol synthesis. Only in recent years have stable commercial catalysts containing copper been available. The combination of lower temperatures and means of stabilization of copper have contributed to the use of this metal in methanol synthesis. These factors have minimized the loss of activity of copper-containing catalysts.

Liquefaction of Coal

Earlier work on hydrogenation of coal to make liquid fuels was attempted by Bertholet and Ipatief [99]. Bergius began his work on coal hydrogenation in 1910 and had a continuously operating system by 1913. Pressed for raw materials for making dyes, BASF, a division of I. G. Farbenindustrie, became interested in coal liquefaction. High-pressure and catalytic technology developed for ammonia and methanol synthesis was helpful in the development of coal hydrogenation processes. Intense effort which began in 1924 led to the development of successful commercial plants which peaked with a production capacity of 100,000 bbl/d by the end of World War II [99]. This is a great technological achievement by any standard. Coal liquefaction was carried out in two stages. In the first stage, coal was blended with a heavy oil from the process and hydroprocessed using "luxmasse" (iron oxide) as the catalyst. In the second stage, light distillate from the first stage was upgraded using sulfides of molybdenum or tungsten promoted by cobalt or nickel sulfides. The principles of operation and the catalysts of the BASF process are used in most of the hydroliquefaction processes that are in the developmental stage today.

Hydrogen/carbon (H/C) ratios of different fossil fuels are compared in Table 3 [100]. A principal difference between coal and petroleum is the H/C ratio. Hence an important factor in converting coal to liquids lies in the addition of hydrogen. As the BASF scientists determined, this can be accomplished readily with the aid of catalysts.

At present, four types of processes are under development for the liquefaction of coal [101]: (1) pyrolysis, (2) solvent refining, (3) Fischer-Tropsch synthesis, and (4) hydroliquefaction of coal. The first two processes do not employ catalysts.

Exxon's donor solvent process (EDS) and H-coal process belong to the hydroliquefaction category [101]. In the EDS process a fraction of the oil produced from the process is catalytically hydrogenated and used as a vehicle oil to transfer the coal into the high-pressure extraction reactor. Here the hydrogen-rich oil fraction transfers its hydrogen to reactive coal fragments, thus producing liquid. Hydrogenation of the vehicle oil is carried out in a separate stage using cobalt-molybdenum catalyst under turbulent conditions.

TABLE 3 Chemical Composition of Some Coals and Petroleum (courtesy of Marcel Dekker, Inc. [100])

	Anthracite	Medium Volatile Bitumen	High Volatile A Bitumen	High Volatile B Bitumen	Lignite	Petroleum Crude	Gasoline	Toluene
C	93.7	88.4	84.5	80.3	72.7	83.87	86	91.3
H	2.4	5.0	5.6	5.5	4.2	11.14	14	8.7
O	2.4	4.1	7.0	11.1	21.3			
N	0.9	1.7	1.6	1.9	1.2	0.2		
S	0.6	0.8	1.3	1.2	0.6	1.0		
H:C atom ratio	0.31	0.67	0.79	0.82	0.69	1.76	1.94	1.14

aCoal analysis on moisture and ash-free basis. Ash content of coal 3 to 15% C-Fraction aromatic = 0.7.

Aromatic rings per cluster not over 3. Harom: Haliph = 0.23. H:C atom ratio of petroleum residua: asphaltenes, 1.18; resin, 1.47; oil, 1.67.

The H-coal process uses a similar concept but the reactor design is different. An ebullient bed is used to make the contact between hydrogen, vehicle oil, coal, and the catalyst.

The University of Utah coal liquefaction process differs from the EDS process and H-coal process in two ways: (1) the reaction time and (2) feeding of the coal into the reactor. Reaction time for the University of Utah process varies from 5 to 100 s compared with 20 min to 2 h for the other processes. No solvent is used to transfer the coal into the reactor. Coal pulverized to -40 mesh is impregnated with zinc chloride (5%) catalyst and fed to the reactor with the aid of hydrogen. Conversions as high as 90% to liquids and gases have been obtained, but the optimum conversion is around 70 to 75%. Operating conditions are: temperature, 450 to 550°C; and pressure, 1600 to 2000 lb/in.².

Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis involves the hydrogenation of carbon monoxide to make higher hydrocarbons. A successful version of this process was attained in Germany in 1925. The primary interest of the process at the time of its discovery was in the production of gasoline from coal and coke. This process and the hydroliquefaction of coal were competitive means for the production of synthetic fuels. An early catalyst used in Fischer-Tropsch synthesis was metallic iron promoted by alkali metal carbonates. Under the high pressures at which this catalyst was operative it produced chiefly oxygenated compounds; at low pressures it lost its activity quickly. The desirability of operating at low pressures led to the development of an active, stable cobalt catalyst which gave high yields of hydrocarbons at atmospheric pressure.

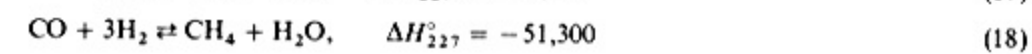
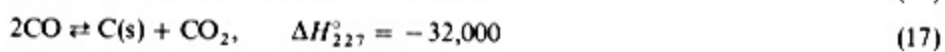
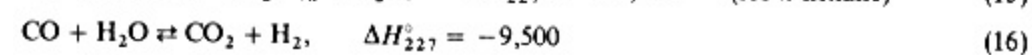
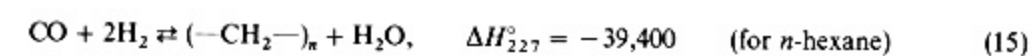
Nine plants based on Fischer-Tropsch technology with a rated capacity of about 700,000 tons/yr were in operation in Germany between 1935 and 1945. This accounted for nearly 20% of the synthetic fuel produced in Germany, the rest coming from the hydrogenation of coal. The catalyst used in these Fischer-Tropsch plants had the following composition: Co:ThO₂:MgO

kieselguhr = 100:5:8:200 [62]. About 75% of the plants operated at atmospheric pressure while the rest operated at 7 to 20 atm. Synthesis gas was produced by water-gas generators using coke or coal. Prior to 1945, commercial plants were licensed to operate in France, Japan, and Manchuria.

With the availability of cheap petroleum after the war, the interest in Fischer-Tropsch synthesis as well as coal liquefaction died. The only commercial plant in operation today is in South Africa at Sasolburg (SASOL I). It has a rated capacity of 240,000 tons of product per year and has been in operation since 1955. SASOL II, with 4 to 5 times higher rated capacity, is planned to go into operation in 1980 [101]. The economics of these plants is justified for the following reasons: (1) the availability of very cheap coal, and (2) South Africa's effort to reduce its dependence on imported oil. SASOL I employs five fixed bed reactors and three fluid bed reactors. The fixed bed reactors operate at 220 to 240°C whereas the fluid bed reactors operate around 240 to 320°C [102]. The active component in both reactors is iron promoted with alkali. The only commercial plant that went into production in this country was by Carthage Hydrocol at Brownsville, Texas. It was commissioned in 1949 and shut down in 1953 because of financial and operational difficulties. The plant never operated at more than 30% of its rated capacity.

Dwindling resources of petroleum have created renewed interest in Fischer-Tropsch synthesis. Production of liquid fuels and olefins from coal using this process is being examined.

Four important reactions taking place in the Fischer-Tropsch synthesis are as follows [103]:



The exothermic nature of these reactions indicates that product formation would be favored by lower temperature. Reaction (15) is the desired reaction; (16), (17) and (18) are unwanted side reactions. Reaction (16) wastes CO. Reaction (17) deactivates the catalyst by the deposition of coke on the catalyst. Reaction (18) wastes both CO and H₂. The change of free energy for all these reactions as function of temperature is given in Fig. 11. Over most of the temperature range, all the unwanted reactions are thermodynamically favored. Therefore, the high selectivity of the catalyst in producing the desired product is essential for the economic success of the process. The mechanism of reaction on the Fischer-Tropsch catalyst and the importance of reactor design are discussed elsewhere [102, 103].

Oxidation of Sulfur Dioxide

Sulfuric acid, which is said to be the workhorse of industry, is manufactured by oxidizing

SO₂ to SO₃ and absorbing it in sulfuric acid. Undoubtedly,

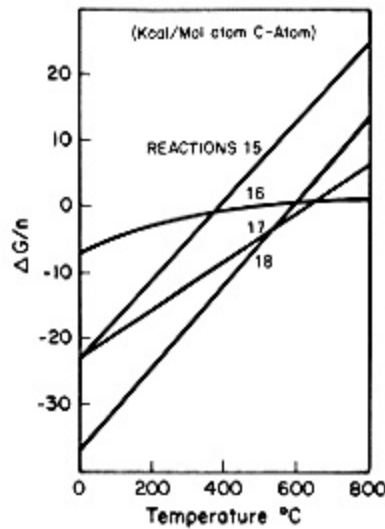
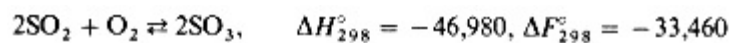


Fig. 11.
Free energy change of the reactions
(per gram atom C during hexane formation)
as a function of the reaction temperature.
(Courtesy of Hydrocarbon Processing [103].)

oxidation of SO₂ is one of the major catalytic processes. Production of sulfuric acid is believed to be a reliable indicator of chemical production of a country. By far the largest user of this important product is the fertilizer industry. (See Table 4.) It is also used as a dehydrating agent, a reagent in chemical processes, an acid, a catalyst, an absorbent, etc. [91].

Oxidation of SO₂ is an exothermic reaction:



Even though pressure would favor the formation of SO₃, all the commercial plants operate at near atmospheric pressures. The gas containing 6 to 10% SO₂ enters the converter at a temperature of 400 to 425°C. The LHSV employed is around 500 to 1000 $\text{V}_g \text{V}_c^{-1} \text{h}^{-1}$ [75]. The catalyst in the converter is separated into several sections with cooling arrangements between sections to remove the heat from the gases. The exit temperature of any section is not allowed to go over 600°C. In fact, the exit temperature of successive beds is decreased progressively to increase the concentration of SO₃ in the exit gases. Conversions of 95+% per pass are common. Plants constructed prior to World War I used iron oxide and platinum as oxidizing catalysts, the latter being used in the final stages of the converter. With the development of vanadium catalyst in the 1920s, the use of iron and platinum declined. Present-day commercial catalyst consists of V₂O₅ supported on silica and promoted by K₂O. Vanadium catalysts are very resistant to poisons (chlorides and selenium are temporary poisons) and have a very long life. Catalyst life of 20 yr without significant reduction in activity has been reported. The catalyst used in commercial operation has 5% V₂O₅ and a molal ratio of potassium to vanadium of about 3.

TABLE 4 Sulfuric Acid-Consuming Industries in the United States (thousands of net tons, 100% H₂SO₄)

(courtesy of Reinhold Publishing Co. [91])

Consuming Industries	1957		1970		1975	
	Tons	%	Tons	%	Tons	%
Fertilizer industries						
Phosphatic fertilizers	4,550	27	13,910	49	16,900	51
Ammonium sulfate or other	1,600	9	2,180	8	2,280	7
	6,150	36	16,090	57	19,180	58
Other industries						
Chemicals	4,400	26	3,090	11	3,830	12
Petroleum refining	2,000	11	1,880	7	1,880	6
Iron and steel	1,020	6	690	2	530	1
Other metals	270	1	710	2	1,300	4
Paints and pigments	1,380	8	1,490	5	1,160	3
Rayon and cellulose film	780	5	860	3	860	3
Miscellaneous	1,120	7	3,580	13	4,260	13
Total	17,120	100	28,390	100	33,000	100

Oxidation of SO₂ has been extensively studied. Unfortunately, there is no unique view on the kinetics and mechanism of this reaction. Quite an array of rate equations have been published in the literature [104]. However, there is general agreement that the reactions are first-order with respect to O₂ and between one-half and one with respect to SO₂. Under the operating conditions a melt is believed to be formed consisting of vanadium compounds dissolved in an alkali pyrosulfate mixture which acts as the catalyst [105]. There is considerable dispute as to the valence state of vanadium under these conditions [106].

The Future of Catalysis

Considering the dependence of fossil fuel and chemical development on catalytic reactions, the future of catalytic technology has never been brighter. Along with this emphasis will come increased research in the fundamental aspects of catalysis.

The outlook for increased understanding of the role of chemisorption and the nature of the bonding between catalysts and substrates is excellent. This will be achieved by utilizing combinations of modern instrumentation with more conventional techniques for examining catalytic phenomena in great depth. The instruments in mind are very expensive so that this mitigates against all but a few of the laboratories engaged in catalyst research having combinations of such techniques as Auger spectrometry, electron spectroscopy-

copy for chemical analysis (ESCA), low-energy electron diffraction (LEED), electron microscopy, X-ray spectroscopy, IR spectrometry, and ultrahigh vacuum. Of particular interest is the ability of these techniques to elicit information about surface atoms. Catalysis is concerned with surface layers of solids, and these are certainly quite different from bulk properties of the corresponding solids. Hence techniques which yield information on the properties and orientations of atoms in the surface layers have to be important in studying catalysts. The number of groups engaged in catalysis research having adequate manpower and funding to acquire and operate many or all of the new techniques must increase if knowledge of catalysis is to ascend to new levels. Analysis of progress in catalysis indicates that significant advances have been made in those instances where a concerted massive attack has been made on a catalyst system employing a multiplicity of techniques including modern instrumentation as well as conventional methods.

Progress in the application of catalysts will continue. New developments include bimetallic catalysts for catalytic reforming, molecular sieve catalysts for many uses, improved catalysts for hydrogen production and methanol production, improved low temperature water-gas shift catalysts, and catalytic selectivity control by molecular size and shape discrimination. The latter property will be expanded into new systems with pore sizes larger than those available in the present molecular sieves.

It is expected that new catalysts and methods will be developed for upgrading coal-derived liquids, methane synthesis, and the Fischer-Tropsch synthesis. Ammonia synthesis catalysts which are capable of lower pressure and lower temperature operation are a target for a number of workers. Such a development may have only limited economic impact on the synthesis of ammonia since present technology is highly efficient and the synthesis step is only a part of the whole. Ammonia manufacture, broadly considered, is a very complex system for making a very pure H_2/N_2 mixture ready for the synthesis step.

Another branch of catalysis with a promising future is that of homogeneous catalysts. As these are better understood and the relationships with heterogeneous catalysis more fully developed, it is to be expected that many of our heterogeneous catalysts systems will be replaced by more controllable homogeneous systems. Examples of this could be in methane and methanol synthesis and oxygenated compound synthesis such as ethylene oxide and glycol.

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Precious Metals Catalysis

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Introduction

A catalyst chemically interacts with reactants to bring about their conversion to desired products while itself remaining unchanged. It is uniquely ironic that the precious (or noble) metals produce some of the most active and selective catalysts yet are also frequently used in applications where inertness or nonreactivity is essential. For example, many materials, such as high-temperature alloys, dental products, electronic components, and surgical implants, use precious metals because of their chemical inertness in severe temperature and/or corrosive environments. Unquestionably, precious metals are unique and indispensable materials for many industrial applications.

This article describes the use of precious metals in industrial catalytic applications.

Precious Metals

The precious metals gold, platinum, palladium, rhodium, iridium, osmium, and ruthenium are often referred to as the noble metals. Silver, although not a precious metal, is also included, particularly for industrial applications. These metals are mined in various locations throughout the world, but the precious metals proper are principally found in the Republic of South Africa. Mines exist in the United States, Canada, Australia, China, the Soviet Union and South America, but their contributions are minor, except for silver. Information on origins, use, and world consumption are available elsewhere [13].

A comprehensive description of the chemistry of these metals and their compounds is discussed in a series of articles published in Coordination Chemistry Reviews (Ru and Os [4], Rh and Ir [5], Pd and Pt [6], Au [7], and Ag [8]). Their metallurgical properties have been described elsewhere [9, 10], and general review articles that describe properties and uses are available [11-14]. Recovery [15, 16] and analysis [17, 18] of precious metals have also been presented.

Catalysis in General

Catalysts and catalyst carriers are described in detail elsewhere [19, 20]. However, a brief description here is useful.

An effective catalyst increases the rate of conversion of reactants to desirable products, yet its net concentration remains unchanged. A given catalyst's physical and chemical properties [21], along with the process

conditions under which it operates, determine the overall reaction rate and product distribution.

Transition metals, comprising both precious and nonprecious metals (base metals), are commonly used active components. Nontransitional materials, such as highly porous, high surface area Al_2O_3 , SiO_2 , TiO_2 , and carbon, are commonly used as supports upon which the active transitional metals or metal oxides are deposited to improve accessibility of the reactants to the active catalytic components. Although general theory [22] and methods of manufacturing [23, 24] commercial catalysts are available, precise preparative details are almost always proprietary and hence not available to the general public. Many patents exist; however, specific details of actual procedures are often not disclosed.

Industrial catalysis primarily involves heterogeneous processes in which the reagents and products exist in a phase different from the catalyst. The heterogeneous catalyst is usually a solid; reactants and products are liquids and/or gases. Continuous processes usually operate in beds in which the catalyst is "fixed"; reactants are passed through the bed and are converted to products. A slurry-phase process, in which the catalyst is mixed with the reactants, is commonly used for batch operations. Both processes allow the catalyst to be easily separated from the reactive mix so it can be reused or, if required, recovered for metal value. The latter is essential for precious metal-containing catalysts and must be factored into the overall economics of the process.

Homogeneous catalysts are dissolved in the reactive mix. For this reason, separation after use is often quite difficult. As a result, precious metals have not found great use as homogeneous catalysts in industrial processes, although some commercial processes exist, particularly in the production of low-boiling, distillable products.

Large volumes of base metal catalysts are used by the catalyst industry for upgrading petroleum into fuels, as well as in processing feeds to make chemicals. Precious metal usage is considerably less than base metals, both for technical and economic reasons; however, processes that operate with them generally require less severe conditions. They tend to have longer lives and, once deactivated, can often be regenerated and reused.

Fuels from Petroleum

Reforming of Naphtha

Crude oil is fractionated into various boiling ranges corresponding to different sets of molecular species. The naphtha range corresponds to that portion of the fractionate boiling between 10 and 200°C and usually includes aromatics, such as benzene, toluene, and xylenes, as well as straight, branched, and cyclic hydrocarbons between 5 and 11 carbons.

These molecules can be further processed into a variety of products, including high-

octane fuel, such as gasoline (Fig. 1), by a process called catalytic reforming. The heart of the process is the catalyst, which en-

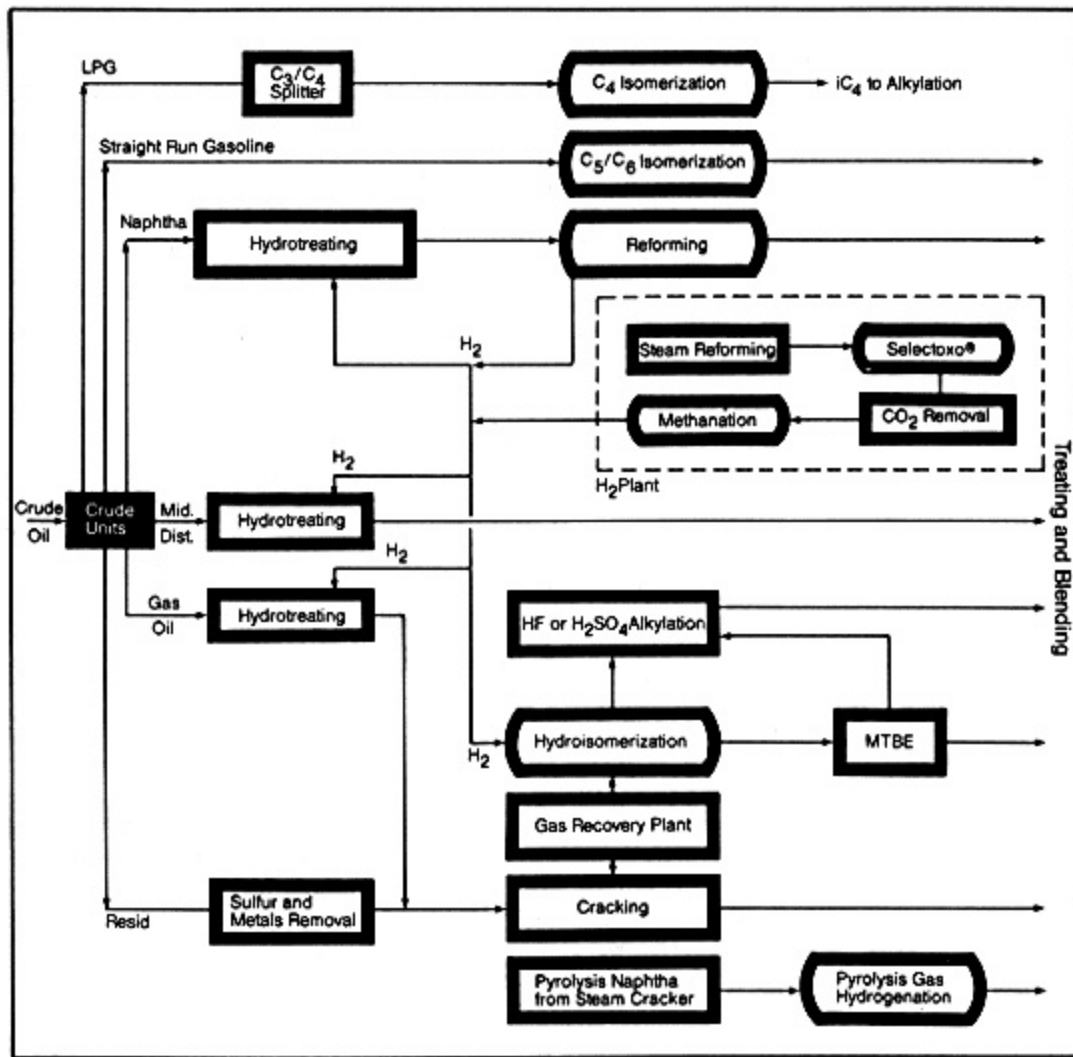


Fig. 1

Petroleum refining. The processes in lozenges are precious metal processes.

hances the conversion rate of "naphtha" molecules to desired products. Alkylated aromatics and branched hydrocarbons represent the higher octane components, and thus catalytic reforming optimizes their production from the naphtha feedstock.

Figure 2 illustrates the principal types of reactions typical of reforming. High-octane products provide enhanced combustion efficiencies in the internal combustion engine, and their presence eliminates the "knock" experienced by motorists.

Platinum, supported on acidified γ - or β - Al_2O_3 , introduced in the late 1940s by Universal Oil Products (UOP) [25] led to substantial improve-

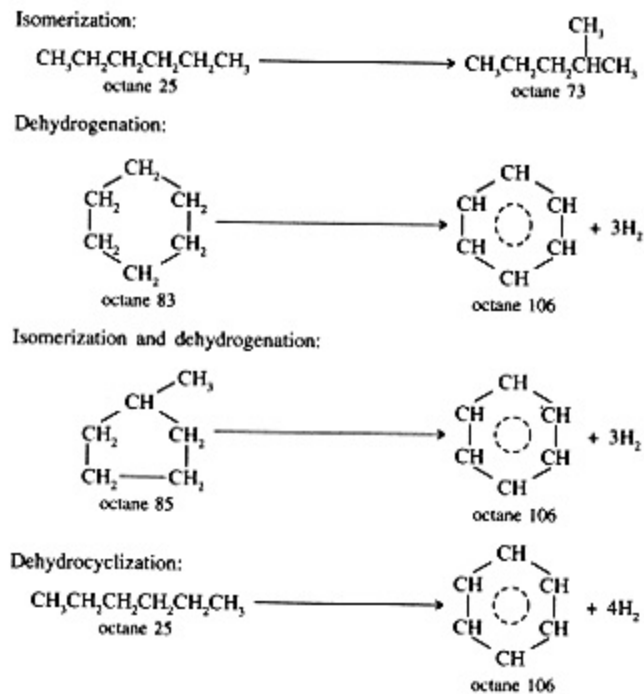


Fig. 2
Model reactions for catalytic reforming.

ments in activity, selectivity, and catalyst life. These catalysts replaced molybdenum-containing catalysts in use at the time. As in many applications, the use of highly active precious metal catalysts greatly reduces the process severity, which in turn contributes to improved selectivity to desired products and catalyst life.

Typically, a catalytic reformer operates [2530] between 480 and 540°C at pressures not exceeding 550 psig. Although catalytic reforming is a hydrogen-producing process, it is necessary to carry it out under a protective atmosphere of hydrogen at elevated pressures to prevent deactivation by coke deposition. The protective atmosphere consisting of H₂ and low carbon number hydrocarbons, produced by hydrocracking, is continuously recycled through the catalyst bed.

The catalyst is most often present as 1/16 in. Al₂O₃ cyclinders (extrudates) or beads into which Pt has been deposited. Primarily, Pt functions to dehydrogenate naphthene molecules to aromatics; the halide-containing acidified Al₂O₃ support rearranges molecular structures by skeletal isomerization and cyclization. This synergistic behavior of metal and support has been, and will continue to be, the subject of continuing research for many years [28, 31].

Hydrogen gas, a valuable by-product of the reforming process, is produced via dehydrogenation reactions. Dehydrogenation can proceed be-

yond the desirable products and lead to heavy carbon-rich hydrocarbons that are deposited within the catalyst pore structure. This unreactive "coke" residue is a major cause of catalyst deactivation. Deposition of coke in the pores increases resistance for the diffusion of naphtha molecules to (or product molecules from) the active catalytic sites, causing a decrease in performance. The acid sites associated with the Al_2O_3 also contribute to the formation of polymeric, carbon-rich materials, otherwise classified as coke. To minimize the undesirable reactions that lead to coke deposition, a delicate balance is required to optimize the Pt metal dehydrogenation function together with the acidity function of the support. Because of this optimization, catalyst composition and its method of preparation have a profound effect on performance. As a result, many catalyst producers retain proprietary, preparative details since many years of expensive research and development were necessary to develop their optimum catalyst. Also, process conditions must be adapted to catalyst and feedstock characteristics for optimum performance.

Most recent catalysts contain such promoters as Re [32, 33], Ir [34, 35], and Sn [36, 37], together with Pt, and there is some evidence that these bimetallic catalysts improve the resistance of Pt to sintering [38, 39] and are more coke tolerant [40-42] than those containing only Pt. These catalysts also differ in their sensitivities to feedstock impurities, such as sulfur compounds [43] and heavy metals known to poison the active catalytic sites.

Comparisons with Pt alone and with other bimetallics have been made. Van Trimont et al. [44] reported improved yields of isoheptanes and aromatics, from a C7 feed, with Pt-Re versus a Pt only catalyst. Reactions of cycloalkanes to aromatics are reported to be more favorable for Pt-Re; Pt-Ir is favored for alkanes to aromatics [45]. The presence of Sn, as a promoter to Pt, is believed to enhance benzene formation, decrease metalcatalyzed hydrogenolysis [46], and possibly increase the rate of hydrogenation of dienes to monolefins [39]. It is specifically used in continuous regenerator reformers (i.e., UOP) since its higher initial performance can be maintained with frequent regenerations.

Numerous research and development programs are in progress toward developing an understanding of bimetallic catalysts, particularly the degree of interaction between Pt and its promoter. There appears to be evidence that some alloying between Pt-Re [43, 47] and Pt-Ir [48, 49] occurs under certain conditions, but Pt-Sn remains unalloyed [50]. The arguments usually vary, based on the individual concentrations of each metal. Typically, the total metal concentration varies between 0.25 and 0.7 wt%. For the most part, Pt-Re-containing catalysts represent the majority of catalysts used commercially, although catalysts differ slightly in composition and method of preparation.

Coke formation is considered a major cause of catalyst deactivation [51]; consequently, many procedures for its removal [29, 52-54] have been and are currently used. The most common regenerative procedure involves slowly adding small amounts of O_2 to N_2 to combust the carbon-rich deposits. Thermocouples monitor the temperature in the catalyst

bed;

the flow and concentration of O₂ in the regenerating gas is controlled to avoid temperature surges that could result in additional catalyst sintering.

Sintering, or agglomeration of the initially small Pt crystallites [55] due to thermal effects, also leads to catalyst activity decay; however, catalyst formulations and improvements in regenerative procedures have increased catalyst lifetimes to as much as 10 years.

Rejuvenation procedures include addition of oxygen- and chlorine-containing compounds to redisperse the sintered Pt to small crystallites [49, 56, 57]. Regenerated catalyst then has performance characteristics similar to those of fresh catalyst.

Poisoning [58] of precious metal-containing catalysts by heavy metal (i.e., Pb, Hg, Te, Cu, and As) compounds is usually irreversible. Fortunately, naphtha feeds are generally free of significant quantities of these metals; however, iron from the system piping can severely hinder the performance of the catalyst. Sulfur compounds, such as mercaptans, strongly adsorb onto Pt, which results in deactivation. In many commercial operations, sulfur guard beds are recommended to maintain a low-sulfur feedstock to the catalyst. Desorption, and thus regeneration, usually occurs during coke burn-off. As a result, this deactivation mode is often reversible.

Performance of the reforming catalyst has also been shown to depend on the degree of hydration of the catalyst support [59]. Too low a moisture level can cause the catalyst to deteriorate; therefore some active aluminas containing water of constitution are used. Too high a moisture level, on the other hand, removes the chloride from the reforming catalyst, thereby accelerating activity loss so that high-octane production is impossible and liquid product yields are reduced. An alternative remedy to controlling the water content is to inject small amounts of chlorine-containing compounds into the feed.

There are approximately 3 million troy ounces of Pt in reformer units throughout the world.

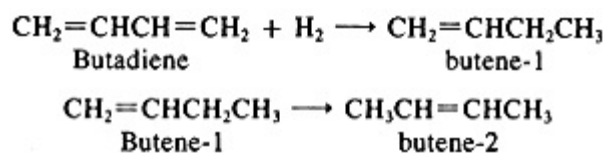
Hydroisomerization

The acid-catalyzed alkylation process (see Fig. 1) combines hydrocarbons, such as isobutane, with olefins, such as butenes, to produce highly branched hydrocarbons used as octane boosters for the gasoline pool. Catalysts are typically AlCl₃, HF, H₂SO₄, or H₃PO₄ [60]. Butenes are therefore common feedstocks to alkylation units. However, they often contain unwanted butadienes and occasionally acetylenes, specifically vinylacetylenes, which must be hydrogenated before entering the alkylation reactors. These diolefinic and acetylenic species increase acid consumption and subsequently increase the waste acid sludge produced in the alkylation process.

Butene-2 is a more desirable alkylating agent than butene-1, since it produces higher research octane number (RON) components, such as trimethylpentane (96.6), rather than dimethylhexane (92.6) [61]. Thus, hy-

hydroisomerization processes have been developed that simultaneously hydrogenate butadiene to butene while maximizing isomerization of butene-1 to butene-2. The product then enters the alkylating units and reacts with isobutane to yield cleaner, higher octane products for the gasoline pool.

The reactions of interest are



It is undesirable to further hydrogenate the olefin to the saturate. Once again, a delicate balance of the dual-function catalyst is required. The metal component must hydrogenate the olefin to the monolefin without overhydrogenating to the saturate; the acidified support must catalyze isomerization of the butene-1 to butene-2. For these reactions the catalyst of choice is usually [62] Al₂O₃-supported Pd [63] prepared commercially according to proprietary procedures.

Process conditions of temperature, pressure, space velocity, and hydrogen-butadiene ratio are varied to produce a product that is low in butadiene or other diolefins, such as propadiene, high in butene-2, and with little loss of butenes to butane by oversaturation. Usually, butadiene concentrations can be reduced below 100 ppm from an initial value of 12 vol%. In addition, approximately 50% of the butene-1 can be converted to butene-2.

Typically this process operates with Pd on Al₂O₃ pellets packed in a fixed-bed reactor at temperatures between 40 and 80°C and pressures close to atmospheric [64-66]. The process is usually conducted in a liquid phase.

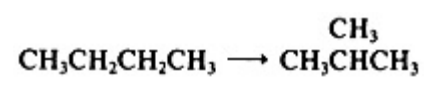
Because of the low hydrogen feedrates, an upflow concurrent floodedbed reactor has proven to be quite successful for good gas-solid-liquid contacting and minimization of polymer formation.

Catalyst deactivation occurs as a result of excessive coke formation, as well as by poisoning, most commonly by sulfur-containing compounds. Regenerations are common, and many plants operate for years with the same charge of catalyst. Ultimately, it must be changed out because of the Pd and Al₂O₃ sintering that occurs during regeneration. Interestingly, some commercial processes actually add impurities to the feed to control the degree of hydroisomerization. These impurities include sulfur-containing compounds, as well as CO and NH₃ [62, 67].

Paraffin Isomerization

The catalyst required to promote skeletal isomerization of butane to isobutane is dual function in nature in that a metal and acid component are necessary to bring about skeletal isomerization [68] reactions (Fig. 1).

CH₃



The metal function is often Pt, which is postulated to initiate dehydrogenation of the paraffin, forming an olefin intermediate. The acid support, which can be Al_2O_3 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, or a zeolite, contributes an H^+ , forming a carbonium ion. Skeletal isomerization occurs, and the Pt catalyzes the hydrogenation of the isomerized olefin, thus forming the branched paraffin. The isobutane is then used as a reactant for olefin alkylation.

Processes usually operate in the vapor phase in fixed-bed reactors at temperatures between 150 and 200°C and pressures between 200 and 400 psig. Cycle life between regenerations for coke removal is approximately 2 years. Depending on feed impurities, such as H_2S , H_2O , and higher hydrocarbons, catalyst life can be as long as 10 years. Feed pretreatment is often used to remove these impurities.

In addition, C_5 and C_6 linear paraffins (RON = 72) can be isomerized to their branched isomers (RON = 85), resulting in improved octane ratings. In general, the catalyst may be Pt on halide-containing alumina or zeolite; however, variations in composition, method of preparation, and activation procedures exist. The Shell Hysomer fixed-bed process [69, 70] utilizes Pt on a strongly acid zeolite (i.e., mordenite). This typically increases the octane number of the feed from 67 to 80 by isomerizing normal pentanes and hexanes to their branched isomers. The dual-function catalyst is believed to operate according to the mechanism already stated [68] between 200 and 600 psig in the vapor phase and at temperatures between 230 and 290°C. Poisons, such as coke, H_2S , benzene, and higher hydrocarbons, are removed during regeneration. Adsorbed poisons, including sulfur compounds and water, can be removed by decreasing their concentration in the feed to 35 ppm or less.

The British Petroleum (BP) fixed-bed vapor-phase process [71, 72] differentiates itself by use of Pt on acid Al_2O_3 catalyst. It operates under slightly less severe conditions, that is, $P < 400$ psig, $T = 160^\circ\text{C}$, but requires the addition of small amounts of chlorides to the feed to maintain support acidity.

It should be noted that the choice of a nonmetallic chlorinating agent is critical. This was substantiated in a study that demonstrated active isomerization catalysts were produced only by chlorine derivatives of methane that contained at least two chlorine atoms per molecule [73]. With frequent regenerations to remove coke and adsorbed sulfur compounds and water, catalyst lives of up to 10 years are possible. Fundamental studies of Pt on zeolites [74] and Pt on Al_2O_3 [75] are available.

Approximately 89,000 troy ounces of Pt are in isomerization units throughout the world.

Hydrocracking

Catalytic cracking converts gas oils boiling over a wide range (200–560°C) to lighter products, such as gasoline, middle distillate (heating oil), light olefins, and paraffins. Cracking processes operate with no added H_2 to the feed. In contrast, mild hydrocracking

converts gas oils as well as more

refractory stocks, such as cycle oil, and vacuum distillate (boiling range 350–550°C) to gasoline range products: diesel, jet fuel, and light gasoline with little or no unsaturation.

The catalysts are dual function and usually comprise a metal supported on acid supports, such as zeolites, and halide-containing Al_2O_3 . These catalysts are easily poisoned by high concentrations of feedstock impurities, such as nitrogen-containing compounds, which chemisorb onto the acid sites, and sulfur compounds, which adsorb onto the metal hydrogenation component. It is also necessary to reduce the moisture content of the feedstock for most catalytic processes.

Consequently, most processes operate with a base metal catalyst as the first-stage hydrotreater [7678], which reduces the nitrogen and sulfur compounds to H_2S and NH_3 , which can be easily removed by stripping. In the second stage, a Pd or Pt on zeolite [7982] catalyst may be used as the hydrocracking catalyst. It may be generally stated that Ni and Mo or Ni and W on Al_2O_3 or zeolite supports are the most commonly used hydrocracking catalysts; however, for a large number of suppliers this composition is proprietary information [83].

Hydrocracking units typically operate at 1,500 psig and 350–425°C and require a substantial supply of hydrogen [82]. Some processes use fluid or ebullating-bed reactors; the recent trend points to fixed-bed downflow reactors.

Palladium use is approximately 200,000 troy ounces worldwide.

Dewaxing Lubricating Oils

Linear paraffinic hydrocarbons in lubricating oils are waxy and crystallize when cooled. Fluidity at low temperatures is important for lubricating oils used in cold climatic conditions. The "pour point" of such oils can be decreased by removing these waxy molecules by solvent extraction [84] or catalytically by using shape-selective zeolite supports [85–87] impregnated with Pt [88].

Linear paraffins can easily enter the pore structure of the zeolite and hydrocrack on the metal/acid sites to a gas. Nonwaxy branched paraffins are prevented from entering because of steric restrictions and thus remain essentially unconverted. This "sieving effect" increases the concentration of nonwaxy hydrocarbons and thereby reduces the pour point of the oil. Pour point reductions from 20°C to -40°C are obtained when Pt on mordenite is used as a fixed-bed catalyst. Processing conditions become more severe as wax content, sulfur and nitrogen compound concentrations, and boiling range of the feed increase. Typically, 280–390°C and 300–1,500 psig are used [87, 89].

Hydrogenation of Aromatics

Aromatics present in kerosene contribute to low smoke point numbers. To minimize the effects of aromatics, a feedstock with 17% aromatics can be

hydrogenated in a fixed-bed reactor (either vapor or liquid phase) with Pt on Al_2O_3 [90] to 1.5 %, with typical operating conditions of 230-300°C and 750-1,000 psig. Improvements in smoke point numbers from 20 to 31 mm are typical [91]. Of the catalysts used in this reaction, nickel is frequently used [92]; however, Rh and Ru are commonly used in chemical applications of ring saturation. These are discussed in the third section of this review.

Oxidation in Fluid Catalytic Cracking (FCC) Regenerator Units

The equilibrium coke level on FCC catalysts decreases with regenerator temperature and results in enhanced activity. During coke burn-off, in the regenerator cycle of an FCC unit, appreciable amounts of CO are generated. Its complete combustion usually occurs downstream of the catalyst phase in the cyclones and flue gas lines. This results in high temperatures, which in turn impact on the materials of construction. To counter this "afterburning" effect, catalysts that promote the oxidation of CO are admixed with FCC catalyst to facilitate more complete combustion in the bed. This raises the bed temperature only slightly, since it has a high heat capacity and mass and promotes more complete coke burn-off. Small amounts of Pt or other noble metals [93-97], deposited either on the FCC catalyst directly or on other supports, which are then blended with the cracking catalyst, are used. These promoters also reduce the CO level emitted from the stack, thereby improving emission quality.

Pyrolysis Gasoline

Ethylene is produced by the nonselective, noncatalytic steam cracking of naphtha. The severity of the process influences the desired product distribution; the more severe, the higher the diolefin content in the liquid byproduct.

Mild cracking produces a liquid with a diene content of about 12% by weight; more severe conditions result in a product with approximately 15-17% by weight diolefins. The product liquid boils between 40 and 220°C, and if stabilized, it can be blended eventually into the gasoline pool. Unsaturated hydrocarbons, such as propadiene, methylacetylenes, isoprene, cyclopentadiene, pentadiene, and others, are notorious gum formers and polymerize downstream on process equipment if not removed. Pyrolysis gasoline catalysts and processes (Fig. 1) are designed to selectively hydrogenate these gum formers to monolefins of less than 0.1 wt%. Palladium [98, 99] and promoted Pd [100] on Al_2O_3 particulates is the most commonly used catalyst for the liquid-phase fixed-bed processes. Catalyst composition is critical to minimize over-hydrogenation of monolefins to the saturates and to retard strong inhibition (poisoning) by adsorption of diolefins or acetylene compounds onto the metal function [100]. The support must have the proper acidity to minimize its contribution to polymerization and eventual coke formation [99]. In addition, the catalyst must

possess sufficient activity to tolerate feedstocks with high sulfur contents ranging to 0.1 wt%, as well as carbon monoxide present in the same range.

Processes operate around 400 psig and at 65°C in the liquid phase. The liquid phase is important because it serves to "wash" away surface-adsorbed impurities, increasing catalyst cycle life. For better vapor-liquid distribution, reactors are usually upflow flooded bed.

Regenerations take place with hot H₂ to remove adsorbed poisons, such as sulfur compounds and water, or by the normal coke burn-off procedures.

Catalytic Heaters

Fuels, such as natural gas, liquefied petroleum gas (LPG), propane, and butane, can be burned oxidatively over catalysts to generate heat. The presence of a catalyst, such as Pt, allows combustion to occur at temperatures lower than that required for a flame, and thus the absence of a flame (radiant heat) allows greater flexibility in providing heat in homes, campers, and offices [101103]. Thus, catalytic heaters are sold commercially for localized heating.

Typically Pt [104] or other noble metals, depending on the fuel [105], are deposited on a large, flat surface, such as SiO₂, Al₂O₃, or ZrO₂ fibers [106]. The catalytic pad is mounted in a canister and the hydrocarbon fuel allowed to diffuse from a manifold to the back side of the pad. Concurrently, air diffuses from the front, creating a fuel/air interface [107] that combusts at the noble metal catalyst surface. An internal ignition source (e.g., electrical hot wire) ignites the mixture during start-up; when combustion is stabilized, the ignition source can be shut off.

The resultant heat radiates from the pad surface. In most units there is no provision for external venting of product gases. As a result, they should be operated with some room ventilation.

European use is more widespread than in the United States. European government regulations require emission control and automatic shutoff features.

Petrochemicals

Ethylene-Derived Petrochemicals

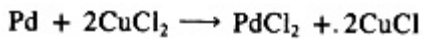
Ethylene and other olefins, such as propylene and butene, are produced primarily by noncatalytic thermal cracking. Feedstocks from which these are derived vary from ethane to naphtha to gas oils, depending on economics, as well as particular product distribution desired. For example, only small quantities of propylene or butene are made when ethane is cracked, but significant quantities are produced when butane, naphtha, or gas oil is used as feedstock.

Acetaldehyde

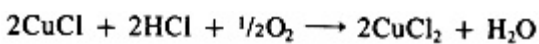
The first commercialized liquid-phase process for the hydration of ethylene to acetaldehyde occurred in the 1950s and was credited to Wacker-Chemie. This catalyst is an aqueous solution of PdCl_2 and CuCl_2 [108] and functions according to a redox mechanism:



The Pd^{2+} is reduced to metallic palladium by formation of an intermediate complex with ethylene. The CuCl_2 is used to reoxidize the Pd:

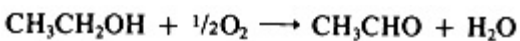


The reduced CuCl is then reoxidized by exposure to oxygen, completing the redox cycle:



In the one-step process [109], the O_2 is directly added to the reaction vessel containing the ethylene, water, and catalyst. The reaction occurs at 125°C and 3 atm. The exothermic heat of reaction distills off the acetaldehyde and water, leaving the dried catalyst to be reoxidized and regenerated for further use.

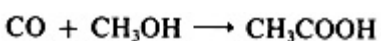
The two-step process [110] operates at 110°C and 10 atm. After the acetaldehyde and water are driven off, air is introduced at 100°C and 150 psig and regenerates the catalyst. The reaction is typically conducted in a lined (i.e., titanium) column reactor [111]. Acetaldehyde can also be produced by the oxidative dehydrogenation of ethanol over a silver gauze or silver needle catalyst at 45 psig and $450\text{--}550^\circ\text{C}$ [112] by



The first step dehydrogenates the ethanol-generating H_2 , which is then oxidized, producing the necessary heat. The reaction is conducted in an adiabatic fixed-bed vapor-phase reactor.

Acetic Acid

Acetic acid was commercially produced in 1960 using a high-pressure, slurry-phase reaction involving the carbonylation of methanol using a homogeneous Co catalyst dissolved in n-butane, according to the reaction



Conditions were quite severe, 250°C and 7,000 psig [113].

During the early 1970s Monsanto commercialized a new liquid-phase process for methanol carbonylation, requiring milder conditions. In this

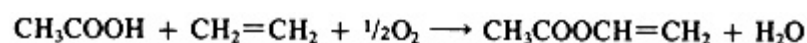
method, a homogeneous RhI_3 catalyst (the active species of which is believed to be $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ [114]) allows the reaction to occur at 175°C , at pressures close to atmospheric. The catalyst is recycled once the desired products are distilled.

It should be noted that deactivation is associated with high solution acidity caused by increasing free HI, leading to formation of $[\text{Rh}(\text{CO})_2\text{I}_4]^-$, which is inactive [115]. Mechanistic studies report this in detail [116, 117].

The annual usage of Rh in 1985 was 6,000 troy ounces.

Vinyl Acetate

Vinyl acetate is the monomer for both polyvinyl acetate and polyvinyl alcohol. It can be produced by vapor- or liquid-phase reaction of ethylene, oxygen, and acetic acid. The vapor-phase reaction is carried out in a fixed-bed tubular reactor and operates at $175\text{--}200^\circ\text{C}$ and 120 psig over a Pd-containing catalyst [118].



The catalyst is typically Pd or Pd + Au on a SiO_2 support. The latter is needed to resist attack by the acetic acid. The presence of small amounts of gold, the use of which is rare in catalysis, is believed to temper the activity of the Pd and avoids complete combustion of the ethylene. The catalyst is poisoned by halide and sulfur compounds.

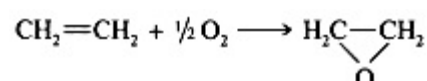
There is some evidence that supported palladium acetate may have been used as a catalyst [119].

The liquid-phase reaction utilizes the Wacker process, described under acetaldehyde, in which Pd and Cu salts undergo a redox process [120]. This reaction is conducted at $100\text{--}130^\circ\text{C}$ but at higher pressures, 450 psig, than the vapor-phase process. Here, the reactor is a fixed bed with multiple tubes for temperature control, and the vessel must be inert (i.e., titanium or stainless steel) because of the corrosive nature of the liquid product.

Approximately 93,000 troy ounces of Pd and 44,000 troy ounces of Au were utilized in 1985.

Ethylene Oxide

Ethylene oxide is produced by selective oxidation of ethylene over a supported silver catalyst.



The catalyst is typically 15% Ag on low surface area α -alumina particulates. To achieve partial oxidation, as opposed to complete combustion of ethylene to CO_2 and H_2O , the catalyst and process conditions must be

carefully designed. The support has a low surface area, and frequently ethylene dichloride is added to the gas stream to partially inhibit the catalytic activity toward complete oxidation [121].

Silver is a unique metal for this reaction because it does not rapidly dissociate O₂. Furthermore, it is postulated that chemisorbed, undissociated oxygen favors the partial oxidation but dissociated oxygen favors complete combustion [122]. Many changes in the catalyst and additives have occurred in this process to improve selectivity and to vary the catalyst size to optimize gas heat-transfer characteristics and to minimize "hot spots" within the reaction tubes.

The process operates with a fixed-bed multitubular reactor at temperatures between 220 and 280°C and pressures up to 450 psig [123]. Processes operate with both air and oxygen, although the latter is most prevalent [124-127]. In each process, recycle is used to optimize selectivity to further minimize the temperature rise in the reactor.

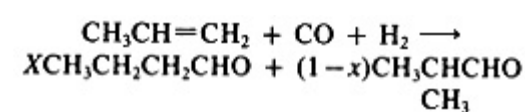
Catalyst deactivation occurs as a result of excessive adsorption of chloride and sulfur compounds and, to a lesser extent, by heavy hydrocarbon deposition. Undoubtedly some sintering of the silver occurs.

More than 7 million troy ounces of silver were used in 1985.

Propylene-Derived Petrochemicals

Aldehydes

The OXO process converts olefins to aldehydes by reaction with H₂ and CO in the presence of a homogeneous catalyst. Since 1938, homogeneous cobalt catalysts [128] have been used to produce a mixture of linear and branched aldehydes (4:1 ratio) at pressures between 3,000 and 4,500 psig and temperatures between 100 and 180°C. The high pressures were required to maintain the cobalt carbonyl complex [129].



Union Carbide, in 1976, commercialized a process for converting propylene to butylaldehyde using a new hydroformulation Rh-containing catalyst [130] HRh(CO)₃[P(C₆H₅)₃].

This catalyst allowed this reaction to be conducted at only 225 psig and 100°C and produced predominantly linear aldehydes (30:1 linear to branched aldehydes), which are much more valuable for producing linear alcohols for solvents and plasticizers. The product aldehydes are volatilized, leaving the catalyst, which can then be recycled. When recovery is necessary, Rh and triphenyl phosphines are extracted with phosphoric acid.

Process details [131] and the reaction mechanism [132] have been reported.

In 1985, 3,000 troy ounces of Rh were believed used.

Butene-Derived Petrochemicals

Butenes

The monolefin butene isomers are produced by the thermal cracking process already described. Butenes can be used as alkylating agents for producing higher octane gasolines (see Petroleum Fuels) or for petrochemical applications within the rubber industry. Butadiene is a gum-forming impurity and can be removed by selective hydrogenation to butenes-1 and 2. The degree of isomerization of butene-1 to butene-2 should be maximized for octane-boosting applications in the petroleum industry. Minimum isomerization is more important for petrochemical applications [133].

The catalyst, typically Pd/Al₂O₃, must be modified slightly according to the desired degree of isomerization. Because precise details of these modifications are proprietary, however, conceptually it can be explained by decreasing the acid nature of the support to suppress isomerization. In addition, process conditions can be modified [134] to vary the selectivity of the reactions.

Reactors are generally upflow flooded bed to ensure good gas-liquid contacting. Reaction conditions vary, depending on feedstock and process objectives, from 40 to 100°C, with sufficient pressure to maintain liquid-phase operation.

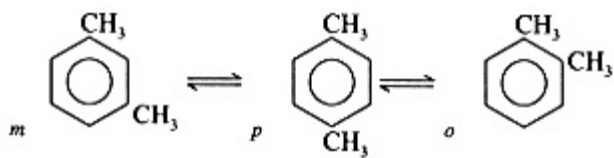
Sulfur compounds in the feedstock decrease catalyst activity. Regenerations with steam and air to remove coke restore activity.

Approximately 24,000 troy ounces of Pd were used in 1985.

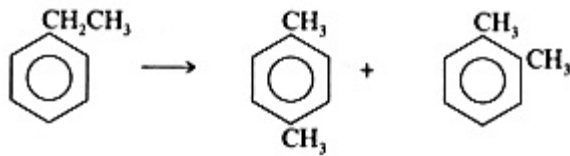
Aromatics

The aromatics, that is, benzene, toluene, and xylenes, produced in naphtha reforming and referred to as BTX, are not only useful in a gasoline blend but, if separated into individual aromatics, become valuable feedstocks for a number of important petrochemical specialty applications.

The xylenes exist in three forms, ortho (o), para (p), and meta (m), and are recovered from reformate.



The o-xylene is a feedstock for phthalic anhydride, p-xylene is a feed for terephthalic acid production: the latter is ultimately converted to polyesters. m-Xylene has little commercial value, and thus there is an incentive to maximize formation of ortho- and para-xylenes from meta. In addition, significant amounts of ethyl benzene (EB) are also present and can be converted to p-xylene.



The catalyst must have a hydrogenation-dehydrogenation and isomerization function. A mixture of $\text{SiO}_2\text{-Al}_2\text{O}_3$ [135] or zeolite [136138] serves as the acid component necessary to produce isomerization; Pt on Al_2O_3 hydrogenates then dehydrogenates to produce the aromatics. This reaction is conducted in a fixed bed at a temperature between 425 and 480°C and a pressure of 200300 psig [135, 139].

Coke burn-off is utilized for regeneration, and catalyst lives of at least 4 years have been reported.

Approximately 12,000 troy ounces of Pt were used in 1985.

Chemicals

Nitric Acid

Ammonia is produced in the Haber process by the catalytic reduction of N_2 with H_2 over a promoted Fe catalyst. The resultant ammonia can then be mixed with air and oxidized to NO over a Pt-rich alloy configured as a wire mesh gauze [140]. After the NO is cooled, it is reacted with excess O_2 to produce NO_2 , which is absorbed in water to produce nitric acid [141], primarily used to manufacture fertilizers and explosives.



Essentially only two catalysts are used throughout the world. The United States favors 90% Pt, 5% Pd, and 5% Rh; the rest of the world uses 90% Pt and 10% Rh, both in the form of wire gauze (Fig. 3). The presence of Pd instead of Rh slightly decreases the installed cost of the catalyst since Pd is traditionally less expensive than Rh; however, no significant performance differences exist [142]. There is a slight increase in cost in metal recovery because of the presence of a third metal.

This reaction is highly exothermic; as a result, gauze temperatures of up to 940°C are common in a high-pressure (100135 psig) plant. Low-(atmospheric) and medium- (4575 psig) pressure plants operate with gauze temperatures up to 850 and 890°C, respectively. Preheat temperatures are typically 250300°C.

The gauzes are stacked in a fixed-bed assembly and operate under bulk mass-transfer control. Gauzes in high-pressure plants are usually no larger than 34 ft in diameter; atmospheric plants operate with large-diameter gauzes, that is, 12 ft.

Typically NO yields of 9495% are obtained in a high-pressure plant. Low-pressure operations can yield up to 98% NO. The production rate in a

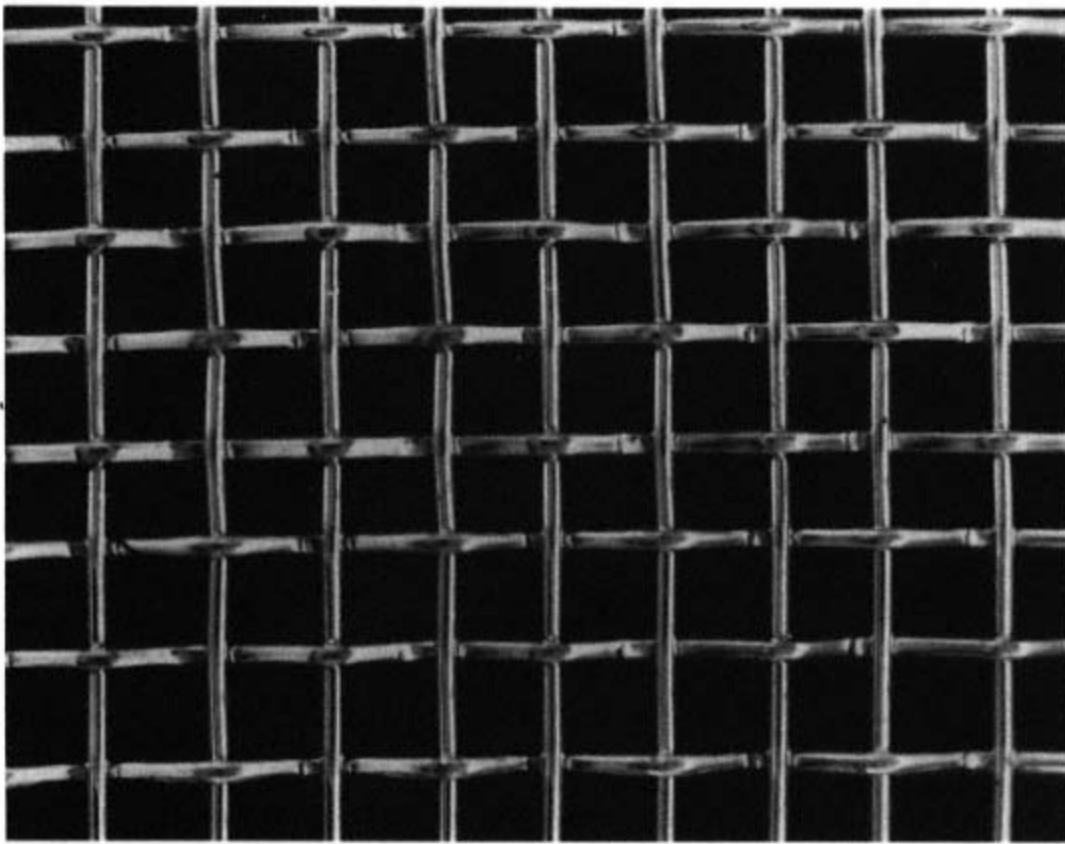


Fig. 3
Unused platinum-rhodium ammonia oxidation gauze.

commercial reactor is approximately 100 tons/day. This corresponds to an average space velocity of $500,000 \text{ h}^{-1}$, or 0.003 s residence time. Because of the very short residence time and reactor bed length, the ammonia and air must be mixed thoroughly before reaching the gauze catalyst. The reactor is downflow and operates adiabatically.

Despite differences in gauze composition, geometry, and size, all undergo a morphological change during use [143]. The gauze sheets are installed as smooth woven wires; after the start of the cycle, however, a phenomenon called sprouting occurs. This causes a considerable increase in the surface roughness and consequently in the surface area. Typically, a fresh, unused gauze has a surface area of $1320 \text{ cm}^2/\text{g}$; after 3 or 5 days in a high-pressure plant, the surface area increases to over $200 \text{ cm}^2/\text{g}$ [144]. This dramatic surface restructuring is shown in Fig. 4.

Accompanying sprouting, or perhaps causing it, there is a loss of Pt from the gauze. This is believed to result from the formation of volatile platinum oxides. Therefore, sprouting occurs because of deposition of

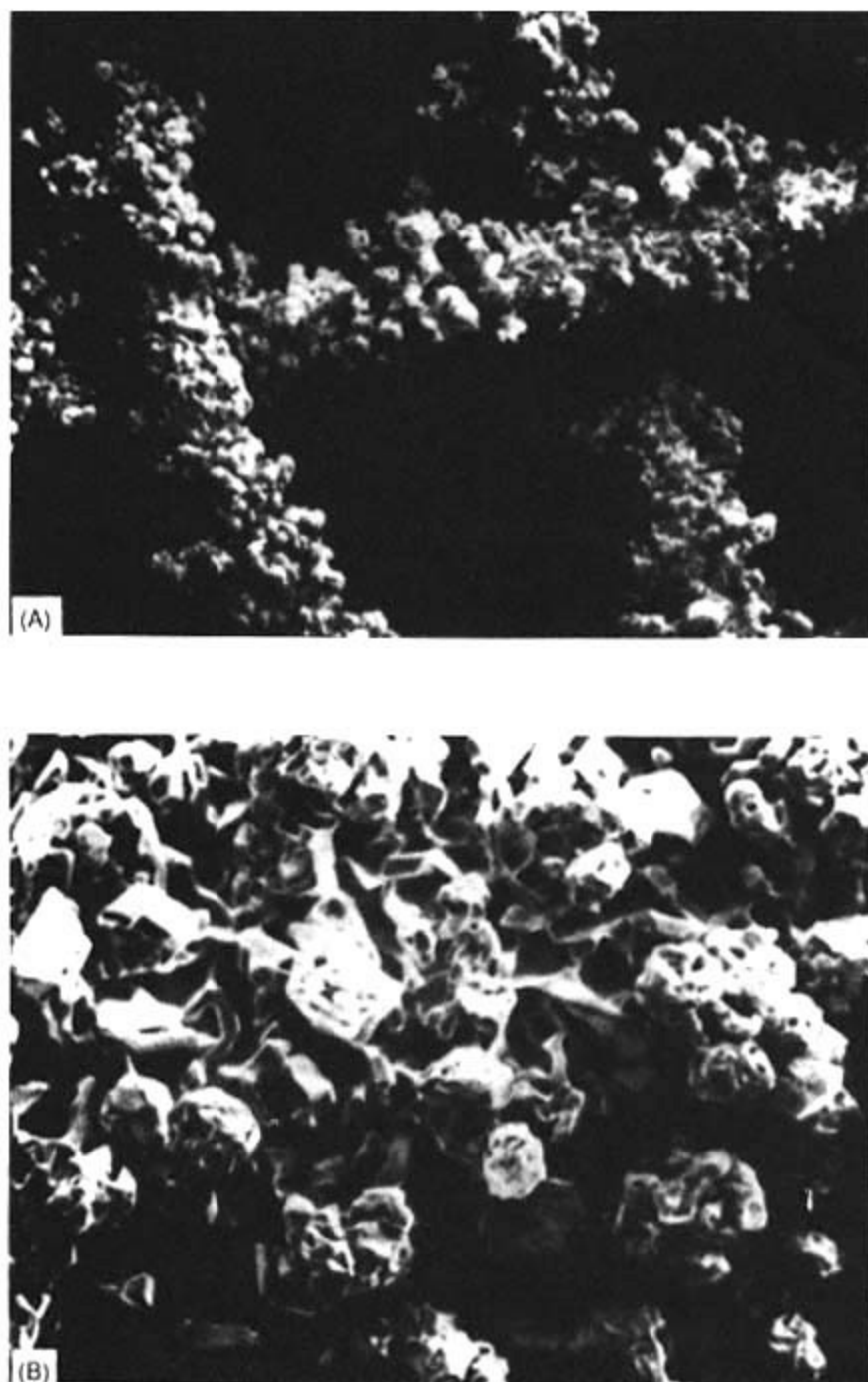


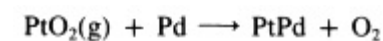
Fig. 4
Platinum-rhodium ammonia oxidation gauze after use: (A) 150 h, magnification $\times 150$; (B) 150 h, magnification $\times 1,000$.

some of the volatile oxides of Pt; however, large amounts are lost to the gas stream. In a 135 psig plant, losses of 0.3 g Pt per ton of HNO₃ produced are common [145].

However, losses decrease with decreasing pressure. The loss of Pt and enrichment of the surface with inactive Rh or Rh₂O₃ is considered a major cause of deactivation. Rhodium oxide enrichment of the surface occurs when the gauze is operated below 850°C. Fouling from deposition of scale from the reactor and piping walls, in particular iron deposition, also contributes to deactivation. For these reasons, the life cycle of the gauze is approximately 23 months in a high-pressure plant and as long as 1 year in an atmospheric unit [145]. Poor mixing of ammonia and air causes severe "hot spots" in the gauze, which can result in actual melting or sagging of the gauze.

Fundamental studies relating composition and selectivity have been reported [146].

The loss of Pt also has a significant impact on the cost of producing nitric acid. Thus, its recovery was an incentive for the development of a Pt recovery process (147). The most efficient recovery process is the use of a Pd-rich alloy gauze located immediately below the oxidation gauze, which "captures" the Pt species. The overall reaction may be represented by



Recovery of Pt involves the dissociation of PtO₂ to its respective elements and formation of an alloy between Pt and Pd. Early recovery gauzes contained 80% Pd and 20% Au and were capable of recovering about 3540% of the Pt evolved. More recently, the Pd content has been increased and it has become recognized that gauze geometry optimization leads to increased recovery efficiencies [148]. Current recovery systems can be designed specifically for each plant. These operate in the mass transfer-limited regime, providing recoveries of up to 80%.

In 1985 over 1/2 million troy ounces of Pt, 11,000 troy ounces of Pd, and 45,000 troy ounces of Rh were utilized for the production of nitric acid. Approximately 60,000 troy ounces of Pd were used for the recovery gauze.

Hydrogen Cyanide

Alumina tubes coated with Pt are used to produce HCN by reaction of NH₃ with CH₄, according to the Degussa process [149]. A multitubular reactor is necessary to provide the external heat for the endothermic reaction, which occurs between 1,000 and 1,200°C with yields of 8090% based on methane.



The Andrussov process [150, 151] operates with a 90 Pt and 10 Rh (wt%) wire gauze similar to that used in nitric acid production, with added

air to combust a small amount of the CH₄ to provide the necessary heat of reaction.

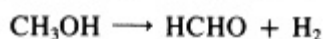


Yields for this process are approximately 70% based on methane. This reactor is a downflow fixed bed that operates adiabatically. Although both processes operate at temperatures in excess of ammonia oxidation, that is, 1,200°C versus 940°C, little Pt is volatilized [152] since the atmosphere is net reducing. Extensive restructuring of the surface occurs [152], however, and its morphology differs considerably from that used for nitric acid (Fig. 5). Deactivation is associated with restructuring of the surface and poisoning from feed components. Hasenberg and Schmidt [153] conducted mechanistic studies on Pt surfaces and found that the carbon layer deposited on the surface enhances the rate of formation of HCN and decreases the decomposition rate of NH₃. The C layer is postulated to react with adsorbed N species to form HCN. The presence of surface iron on the catalyst, either as a catalyst manufacturing impurity or by in situ deposition, substantially affects the catalyst performance [154].

Annual use (1985) was 36,000 troy ounces Pt and 4,000 troy ounces of Rh.

Formaldehyde

Methanol is converted to formaldehyde by either of two processes that both operate outside the explosive limits of methanol and air. Silver needles, gauze, or combinations are used for the oxygen-lean process [155, 156]. The following reactions are believed to occur simultaneously:



The first reaction is highly exothermic and provides the heat for the second endothermic reaction. The formaldehyde process is adiabatic and is carried out in a downflow shallow, wide fixed-bed reactor between 600 and 700°C at close to atmospheric pressure. Typical space velocity is approximately 100,000 h⁻¹, with a reactor residence time of approximately 0.01 s. Yields range from 80 to 90%.

It is believed that the operative mechanism [157159] requires that CH₃OH adsorb onto the silver surface containing preadsorbed oxygen.

The catalyst is sensitive to heavy metals, such as Fe, halogens, and S. Any coke that forms can be easily separated from the catalyst by screening during maintenance.

Over 7 million troy ounces of silver were used in 1985.

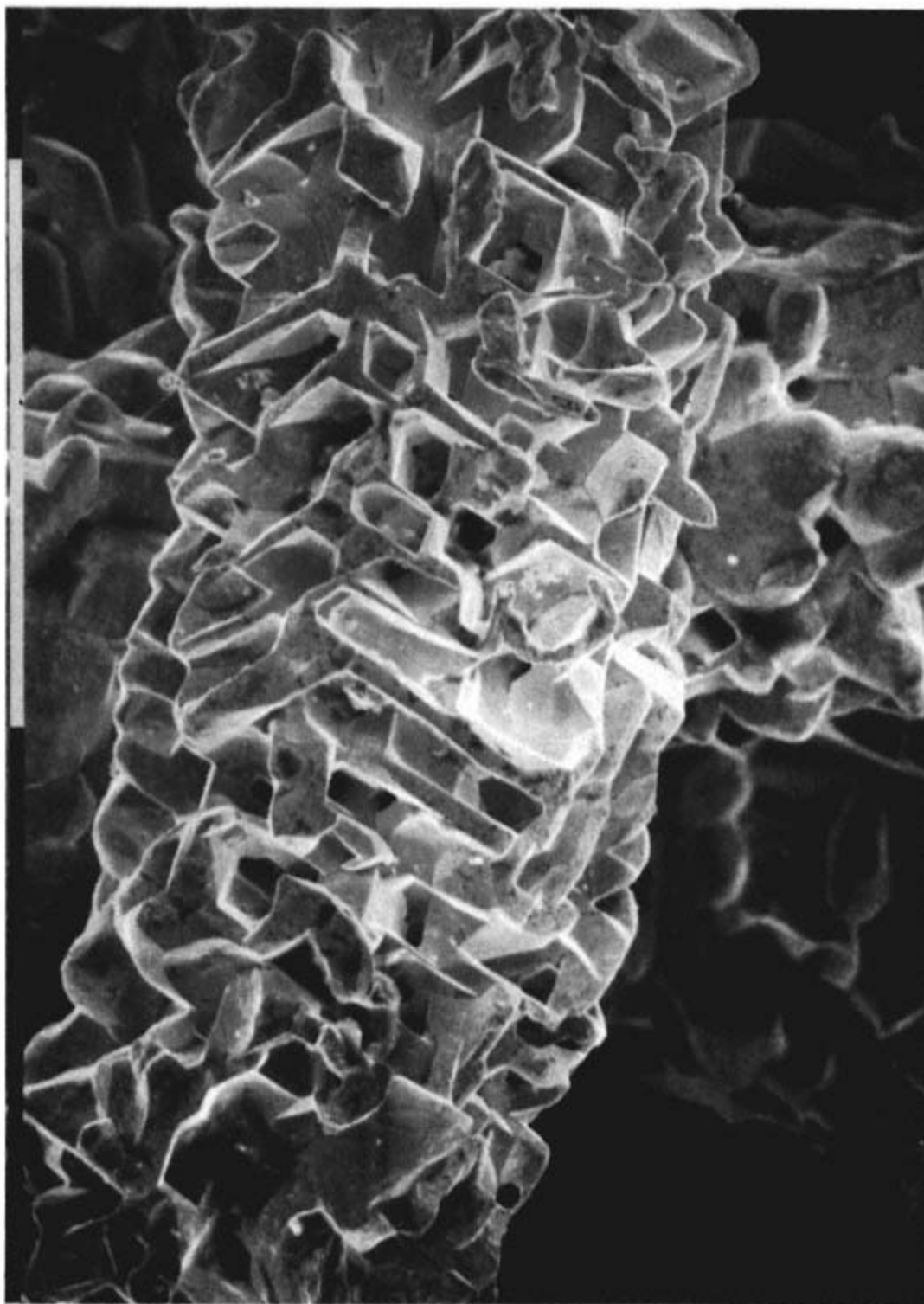
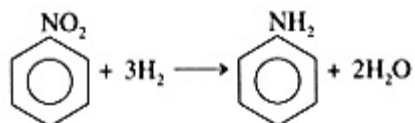


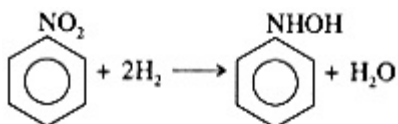
Fig. 5
Platinum-rhodium gauze after use in production of HCN.
(Magnification $\times 1,000$. Photograph compliments of Dr. Ted Koch, duPont.)

Hydrogenation of Functional Groups

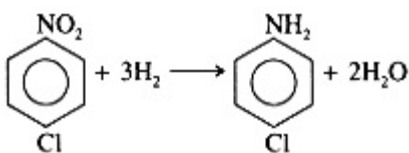
Precious metal catalysts find their most diverse uses in the hydrogenation of a wide variety of functional groups present in organic molecules [160163]. A significant number of these hydrogenations are carried out in slurry-phase autoclave batch reactors [164, 165] using precious metals supported mostly on powders of carbon and, less frequently, on alumina or silica. The choice of metal and support depends very much on the nature of the functional group, other functional groups present on the parent molecule, and, naturally, the desired product. For example, hydrogenation of nitrobenzene to aniline is most commonly carried out with 5% Pd/C:



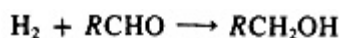
If Pt/C is used for hydrogenating nitrobenzene at 85°C and 800 psig, one produces the corresponding hydroxylamine:



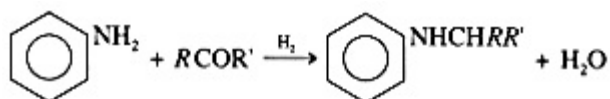
When a halide is also present on the ring, Pt/C is preferred because Pd tends to facilitate dechlorination:



Ring saturation of aniline for the production of cyclohexylamine is accomplished with Rh or Ru catalysts. Ruthenium is also preferred for the hydrogenation of aldehydes to alcohols under mild conditions of 160°C and 700 psig (R = alkyl group).

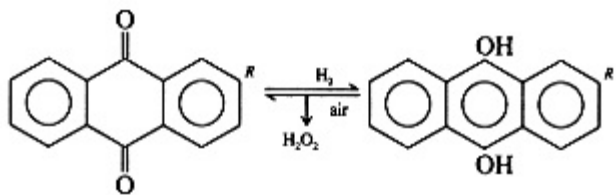


Reductive alkylations are most commonly achieved with Pt/C.



Palladium on Al₂O₃ catalysts is used for slurry and fixed-bed processes for the production of H₂O₂. The catalytic step involves the hydrogenation

of anthroquinone to hydroanthroquinone followed by noncatalytic air oxidation to give H_2O_2 and the starting compound anthroquinone.

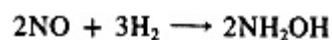


The slurry-phase process utilizes a powdered Pd on Al_2O_3 catalyst that has been treated with alkali that is, sodium carbonate, to neutralize the acidity of the Al_2O_3 [166]. The process is carried out at temperatures less than 100°C and at pressures slightly above atmospheric. The extent of hydrogenation reaction is limited to 50% to avoid oversaturation. The catalyst is then separated and the resultant hydroanthroquinone-rich working solution is air oxidized, producing the H_2O_2 . The H_2O_2 is extracted with water and the working solution recycled.

The catalyst for the fixed-bed process is also Pd but on a particulate Al_2O_3 comprised of only δ and θ crystalline phases [167].

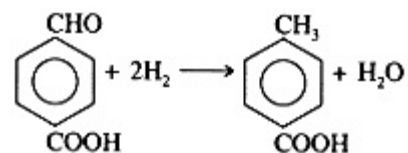
Deactivation occurs primarily as a result of adsorption by organic impurities. Regeneration by washing techniques is practiced [168].

Another important process is the hydrogenation of nitric oxide for the production of hydroxylamine. The latter is an intermediate in the production of nylon.



The reaction is carried out in the slurry phase utilizing a Pt on carbon powdered catalyst at 5°C and atmospheric pressure [169]. The reaction is carried out in dilute HCl solution at a pH not exceeding 2.25 and with an NO/ H_2 ratio between 1:2 and 1:3. Yields of approximately 70% hydroxylamine based on 75% conversion of NO are typical.

Polymer-grade terephthalic acid (TPA), produced by air oxidation of p-xylene, must be free of 4-formylbenzoic acid (color bodies) before conversion to polyesters. Crude acid is dissolved in water and then purified by hydrogenation to remove color bodies. A fixed-bed 0.5% Pd on granular carbon [170, 171] is used to hydrogenate the aldehyde functional group to toluic acid. The latter remains in solution during the crystallization of pure TPA.



The fixed-bed reaction is carried out in an aqueous solution at a temperature of 250°C and a pressure of about 600 psig.

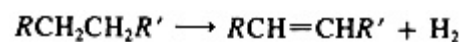
Deactivation occurs as a result of Pd sintering and Pd metal loss caused by attrition of the granular carbon.

The literature on precious metal catalysts in organic synthesis [160165] is too extensive to be covered here; however, the model reactions and corresponding precious metals recommended in Table 1 should be useful as a general guide.

There are many subtleties in selective hydrogenation technology, especially for the carbons used as supports, or carriers, for precious metals. Carbons are derived from a wide variety of material sources, such as woods, coal, peat, and shells. Thus, their physical and chemical properties vary significantly. Pore structures, ash content, and surface functional groups all have a profound influence on the distribution of precious metals and consequently their performance. Furthermore, it is believed that the surface functional groups participate in some steps in the catalytic process. Consequently, a number of precious metal carbon systems must be evaluated when seeking the optimum catalyst [172].

Dehydrogenation

Olefins are far more reactive than paraffins because of their π bond electrons. Thermodynamically, H_2 is added to olefins to form paraffins. This is more easily accomplished than the reverse procedure because of this reactivity. Consequently, dehydrogenation reactions require higher temperatures than hydrogenation reactions.

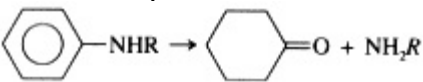
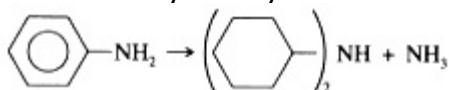
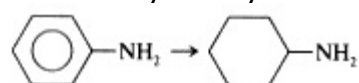
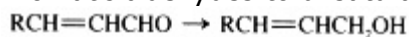
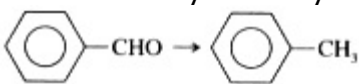
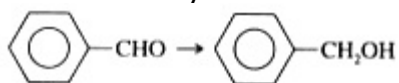
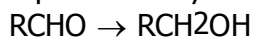
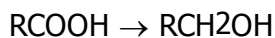
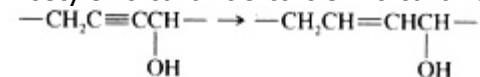


Low-molecular-weight hydrocarbons are most often converted to olefins via thermal cracking processes. Above C_6 hydrocarbons, dehydrogenation to olefins, cycloolefins, or aromatics occurs with the aid of a catalyst. Most are nonprecious metal materials, such as Cr_2O_3 on Al_2O_3 or MoO_2 on Al_2O_3 . However, there are some applications that utilize precious metal catalysts. Cycloparaffins and polynuclear hydrocarbons can be dehydrogenated to the corresponding aromatics using Pt or Pd supported on carbon at temperatures in excess of 200°C [173].

A very important application of a supported Pt catalyst is the dehydrogenation of straight-chain hydrocarbons C_5C_8 for the production of linear monolefins. Straight-chain olefins are used to alkylate an aromatic; the resultant product is sulfonated to alkylarylsulfonates for use in detergents. The key in the design of a suitable catalyst is to diminish the acidity to prevent undesirable reactions, such as cracking, isomerization and aromatization. Thus, the support must be essentially neutral. This can be accomplished by calcining [174] or adding alkali [175] to the carrier to neutralize acid sites.

TABLE 1 Functional Group Hydrogenations Using Various Precious Metals

Reaction	Recommended Metals
Acetylenes	
Acetylenes to cis-olefins $-\text{C}\equiv\text{C}- \rightarrow -\text{CH}=\text{CH}-$	Pd
Acetylenes to paraffins $-\text{C}\equiv\text{C}- \rightarrow -\text{CH}_2\text{CH}_2-$	Pd
Acetylenic carbinols to olefinic carbinols $-\text{CH}_2\text{C}\equiv\text{CCH}- \rightarrow -\text{CH}_2\text{CH}=\text{CHCH}-$ <div style="display: flex; justify-content: space-around; width: 100%;"> <div style="text-align: center;">OH</div> <div style="text-align: center;">OH</div> </div>	Pd, Rh
Acids	
Acids to alcohols $\text{RCOOH} \rightarrow \text{RCH}_2\text{OH}$	Re, Ru (high pressure)
Aldehydes	
Aliphatic aldehydes to alcohols $\text{RCHO} \rightarrow \text{RCH}_2\text{OH}$	Ru
Aromatic aldehydes to alcohols 	Pd
Aromatic aldehydes to hydrocarbons 	Os, Re, Pt (inhibited)
Aromatic aldehydes to unsaturated alcohols $\text{RCH}=\text{CHCHO} \rightarrow \text{RCH}=\text{CHCH}_2\text{OH}$	
Anilines	
Anilines to cyclohexylamines 	Rh, Ru
Anilines to dicyclohexylamines 	Pd, Pt
Anilines to cyclohexanones 	Pd



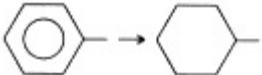
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TABLE 1 Functional Group Hydrogenations Using Various Precious Metals

Aromatics

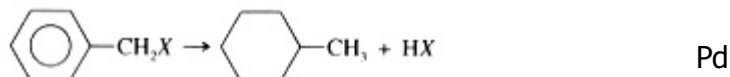
Saturation of carbocyclic and heterocyclic aromatics



Rh, Pt;
Ru, Pd
(elevated pressure)

Benzyl compounds

Benzyl compounds to aromatic hydrocarbons



$X = -OH, -OR, -OCOR, -Cl, -Br, -NH_2, -NHR$, others

Benzyl compounds to cyclohexyl derivatives



$X = -OH, -OR, -OCOR, -Cl, -Br, -NH_2, -NHR$, others

Dehydrohalogenation

Aliphatic and aromatic halocompounds



$X = Cl, Br, I$

Pd

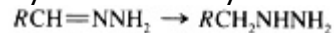
Epoxides

Epoxides to alcohols



Hydrazones

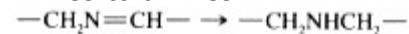
Hydrazones to hydrazines



Pt

Imines

Imines to amines



Pt

Ketones

Aliphatic ketones to alcohols



Aromatic ketones to aromatic alcohols



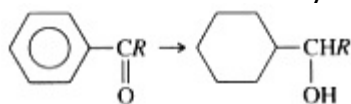
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TABLE 1 (continued)

Reaction

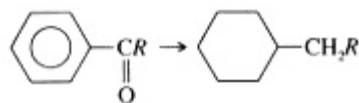
Recommended Metals

Aromatic ketones to alicyclic alcohols



Rh, Ru

Aromatic ketones to alicyclic hydrocarbons



Pd

Nitriles

Aliphatic nitriles to primary amines



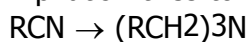
Pd, Pt, Rh

Aliphatic nitriles to secondary amines



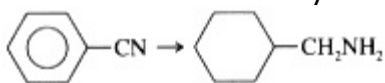
Rh (unreactive solvent)

Aliphatic nitriles to tertiary amines



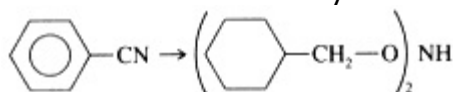
Pd, Pt (unreactive solvent)

Aromatic nitriles to benzylamines



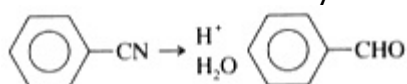
Pd

Aromatic nitriles to dibenzylamines



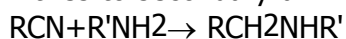
Pt

Aromatic nitriles to aldehydes



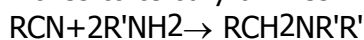
Pd

Nitriles to secondary amines



Rh

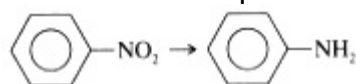
Nitriles to tertiary amines



Pd, Pt

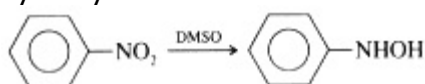
Nitro compounds

Nitroaromatic compounds to anilines



Pd

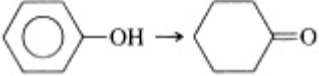
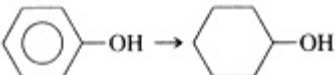
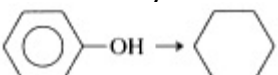
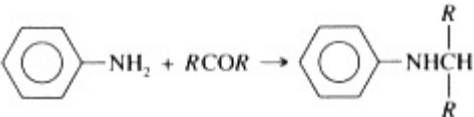
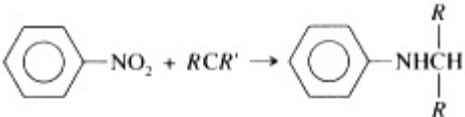
Nitroaromatic compounds to aromatic hydroxylamines



Pt

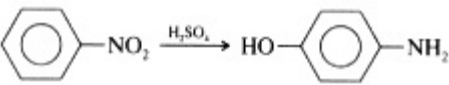
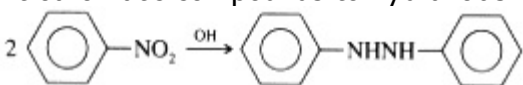
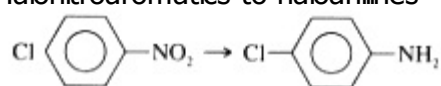
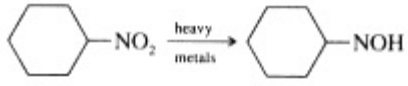
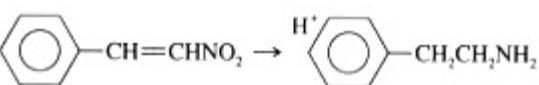
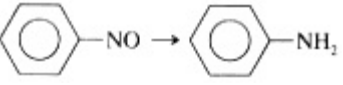
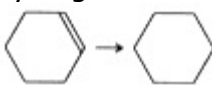

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TABLE 1 (continued)

Reaction	Recommended Metals
Saturation of vinyl compounds $-\text{CH}=\text{CHX} \rightarrow -\text{CH}_2\text{CH}_2\text{X}$	Ru, Rh
Hydrogenolysis of allylic compounds $-\text{CH}=\text{CHCH}_2\text{X} \rightarrow -\text{CH}_2\text{CH}_2\text{CH}_2\text{X} + \text{HX}$ $\text{X} = -\text{OR}, -\text{OCOR}, -\text{Cl}, -\text{Br}, -\text{NHR}$ others	Pd, Pt
Saturation of allylic compounds $-\text{CH}=\text{CHCH}_2\text{X} \rightarrow -\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$ $\text{X} = -\text{OR}, -\text{OCOR}, -\text{Cl}, -\text{Br}, -\text{NHR}$ others	Ru, Rh
Oximes	
Oximes to primary amines $>\text{C}=\text{NOH} \rightarrow >\text{CHNH}_2 + \text{H}_2\text{O}$	Rh
Oximes to secondary amines $>\text{C}=\text{NOH} \rightarrow (>\text{CH}-)_2\text{NH}$	Pd
Oximes to hydroxylamines $>\text{C}=\text{NOH} \rightarrow \text{CHNHOH}$	Pt
Phenols	
Phenols to cyclohexanones 	Pd
Phenols to cyclohexanols 	Rh, Ru
Phenols to cyclohexanes 	Pt, Ir
Reductive alkylation	
Anilines to substituted anilines 	Pt
Nitro compounds to substituted anilines 	Pt
Rosenmund reduction Acid chlorides to aldehydes $\text{RCOCl} \rightarrow \text{RCHO}$	Pd (often inhibited by additives)

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Reaction	Recommended Metals
Nitroaromatic compounds to aminophenols	
	Pt
Nitroaromatic compounds to hydrazobenzenes	
	Pd
Halonitroaromatics to halobenzenes	
	Pt; Pt, Rh (sulfided)
Nitrocyclohexanone to cyclohexanone oximes	
	Pd
Nitroolefins to saturated amines	
	Pd
Nitrosoamines	
N-nitrosoamines to hydrazines	
$>\text{NNO} \rightarrow >\text{NNH}_2$	Pd
Nitrosoaromatics	
Nitrosoaromatics to anilines	
	Pd
Olefins	
Mono-olefins to paraffins	
$-\text{CH}_2\text{CH}=\text{CHCH}_2- \rightarrow -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	Pd
Diolefins to mono-olefins	
$-\text{CH}=\text{CH}-\text{CH}=\text{CH}- \rightarrow -\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-$	Pd
Hydrogenation of cyclohexanes	
	Pt, Rh
Disproportionation of cyclohexanes	
	Pd
Hydrogenolysis of vinyl compounds	
$-\text{CH}=\text{CHX} \rightarrow -\text{CH}_2\text{CH}_3 + \text{HX}$	Pd, Pt

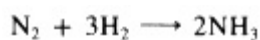
The PACOL process (UOP) is carried out in a vapor-phase fixed-bed reactor at temperatures between 400 and 600°C [176]. A typical liquid hourly space velocity is 4 ml/h/ml. It is common practice to include other promoters in the final catalyst [177, 178]. Hydrogen is used as a diluent gas to minimize coke formation; steam is also added to the feed gas.

Dehydrogenation of light paraffins, that is, LPG to propylene and butenes, have been reported and also utilize a Pt-containing catalyst similar to that used in the PACOL process [179, 180].

Deactivation is dependent on feedstock purity and the extent of coke deposition. Regeneration by burn-off is common. A general review of dehydrogenation of polycyclic hydroaromatic hydrocarbons showing the use of precious metals is available [181].

Ammonia Cracking and Oxidation

Ammonia is produced by the Haber process over an Fe catalyst, according to the simple reaction



When the reverse reaction takes place, H₂ is liberated. Thus liquefied ammonia can act as a convenient "carrier" of H₂. Cracking or decomposition of ammonia, when coupled to a H₂ purification membrane system, has found use primarily for metallurgical and electronic applications for generating pure heat-treating gases. A 0.5% Ru on Al₂O₃ catalyst operating at 800-900°C has been shown to be most effective [182] for this reaction.

It has also been used for launching meteorological balloons and for propulsion applications.

A unique device that simultaneously oxidizes and cracks NH₃, producing a N₂ and H₂ mixture, was developed in the early 1950s [183]. By carefully controlling the NH₃/O₂ ratio above stoichiometric, one can oxidize the NH₃ to N₂ as well as crack the excess NH₃ to N₂ and H₂ over a Pt on Al₂O₃ catalyst. The reaction is initiated by a resistance heater and operates at approximately 500°C. A trace of NO is produced and can be removed by adding O₂ to a second catalyst bed comprised of Pd on Al₂O₃, where the H₂ reacts with the O₂ and NO at 100°C, removing them to acceptable low levels.

This device was used for generating controlled atmospheres of N₂ and H₂.

Sulfuric Acid

Supported Pt catalysts are no longer used commercially for this application and have been replaced by the less expensive V₂O₅-based catalyst. Platinum on SiO₂, kieselguhr (diatomaceous earth), and various sulfates were used in the past.

Gas Purifications

Trace Impurity Removal

Although traces of O_2 are common in many industrial gases, its removal is often essential for their special end-use applications. Small amounts of O_2 (up to 3%) present in H_2 can be combusted initially at room temperature or below by catalysis over a Pd on Al_2O_3 catalyst. In the same manner, small amounts of H_2 (~6%) can be removed from O_2 [184, 185]. The presence of other gas impurities, such as CO and H_2O , can interfere with the catalytic reaction. Increasing temperatures are required as the concentration of CO and H_2O increase. Traces of tritium can also be removed from nuclear reactor off-gases [186] and the resultant T_2O appropriately absorbed from the gas stream.

Oxygen present in streams other than those containing H_2 can also be removed catalytically. The catalyst and conditions depend on other species present. For example, oxygen present in such gases as N_2 , He, Ar, or CO_2 used for generating inert atmospheres is removed using Pt on Al_2O_3 at room temperature by the addition of a stoichiometric amount of H_2 [187, 188].

Traces of carbon monoxide [189] or hydrocarbons [190] in a stream of air are removed by oxidation over a Pt on Al_2O_3 catalyst (or Pt on SnO_2 for laser applications [191]) at slightly above ambient temperatures. The kinetics of these reactions have been described [192-194]. In these reactions, the gases present are impurities; however, systems in which injection of a reductant or oxidant is used are also available. Reactions are usually conducted in vapor-phase fixed-bed reactors using particulate catalysts. Space velocities range from 1,000 to 10,000 h^{-1} depending on the level of removal required of the impurity (99.99 versus 90%), respectively.

Acetylenes are sometimes present in gas streams produced from cracking reactions. Often, these streams are designated for use when generating synthesis gas for chemical production. Acetylenic materials are notorious coke precursors and lead to catalyst deactivation. Furthermore, they can be explosive. Acetylene removal to 10 ppm can be accomplished in hydrogen-containing streams, containing a few hundred ppm acetylene, by hydrogenating acetylene to ethylene or ethane using Pd on Al_2O_3 catalysts [195] with processes operating between 100 and 200°C and moderate pressures of approximately 200 psig. Fixed-bed vapor-phase reactors are used with particulate catalysts. Space velocities range from 5,000 to 10,000 h^{-1} .

Deactivation is usually caused by such impurities as heavy metals, that is, Fe, Sn, and Pb, and acid gases, halides, and sulfur compounds.

Catalyst poisons, such as sulfur compounds, ammonia, alcohols, and coke, can be removed from the catalyst by a controlled air (or diluted air) calcination at 500°C [196].

Purification of H₂ Streams

Traces of CO can be economically removed from H₂ by methanation over a 0.5% Ru/Al₂O₃ catalyst at temperatures in excess of 180°C [185]:



This purification step is required for H₂ to be used in the production of NH₃, since oxygen-containing molecules are poisons for iron-based ammonia synthesis catalysts. This technology is practiced in some ammonia plants. If the CO content of the gas is high (~0.20.3%), however, economics indicate loss of H₂ in methanation (3 mol H₂ per mol CO) is too great a penalty for purification. Thus, alternative technologies have been developed. One such technology is Selectoxo.

Carbon Monoxide Removal from Hydrogen by Selectoxo

The Selectoxo process of Engelhard Corp. [197199] centers on a unique promoted Pt on Al₂O₃ catalyst that permits selective oxidation of CO (~0.5%) in the presence of large amounts of H₂ (~55%) and CO₂. Its major use is purification of H₂ for ammonia synthesis [200].

Small amounts of CO break through the low-temperature shift catalyst in the front end of an ammonia plant. Since CO poisons the ammonia synthesis catalyst (i.e., Fe), its removal is necessary. The Selectoxo catalyst unit is located between the low-temperature shift catalyst and the CO₂ removal system. Stoichiometric amounts of O₂ (as air or occasionally pure O₂) are injected into the stream. The high selectivity of the catalyst converts the CO to CO₂ with essentially no consumption of H₂. This is more economical than reacting 3 mol H₂ with 1 mol CO, producing CH₄, since no H₂ is lost, resulting in as much as a 35% increase in NH₃ yield [200].

The vapor-phase fixed-bed process utilizes particulate catalysts and operates at about 50°C in high relative humidities and pressures averaging 400 psig. Carbon monoxide outlet concentrations as low as 10 ppm are achieved.

The catalyst can be readily regenerated by proprietary techniques when deactivated by amines or alcohols present in the feed (i.e., produced in a low-temperature shift reactor). Halides are also potential poisons.

Ozone from Jet Aircraft Cabin Air

Air fed to the passenger cabin of modern high-altitude commercial aircraft can contain ozone in the parts per million (ppm) level. Ozone in ambient cabin air has been found to be a causative factor for headaches, eye, nose and throat irritations, and chest pains experienced by flight personnel and passengers [201]. Federal Aviation Administration (FAA) regulations require that aircraft cabin ozone concentrations cannot exceed 0.1 vppm (sea level equivalent) on a time-weighted average [202]. Ozone is a very reactive substance and can be decomposed catalytically as well as thermally

[203]. Figure 6 depicts the catalytic advantage over a range of typical operating temperatures.



If air is used from the compressor of the jet engine at higher temperatures (i.e., higher stage of compression), then a substantial jet engine efficiency penalty is imposed. Higher temperatures would be required to thermally decompose the ozone. Catalysts, on the other hand, permit the decomposition reaction to occur at much lower temperatures.

To date, although many catalytic materials, both precious and base metals have been explored for this application, the most effective is palladium on Al_2O_3 supported on a monolith [204, 205].

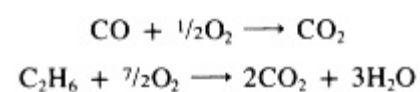
Each converter must be designed to meet the particular requirements of the airplane in which it will be used. Variables include airflow rate, temperature, pressure, allowable pressure drop, and the particular shock and vibration patterns that the converter will experience in service. Design space velocities range from 200,000 to 500,000 h^{-1} . Inlet temperatures are typically 200°C .

Deactivation occurs due to such impurities as S and P compounds present in the airport environment. The ozone itself actually inhibits the reaction by modifying the catalytic surface and changing the catalyst valence state.

Environmental

Automobile Exhaust Purification Catalyst

The 1983 federal emission standards, enacted in 1970 as the Clean Air Act, called for less than 3.4 g CO per mile and 0.41 g hydrocarbon per mile emitted from the internal combustion engine of the automobile. This represents nearly a 90% reduction in pollution emissions from an uncontrolled vehicle [206]. Because of this mandate, many research and development laboratories throughout the world explored possible catalyst systems to meet these rigorous federally imposed standards for vehicles sold in the United States starting with model year 1975. Typical model reactions for which catalysts were needed were



Combustion of gasoline-air mixtures in the engine is incomplete, creating such pollutants as CO, and low-molecular-weight hydrocarbons that is, methane, ethane, ethylene, propane, and propylene. Typically, the exhaust gas stream contains between 1 and 2% CO, 0.050.1% hydrocarbons, 12% CO_2 , 10% H_2O , 0.010.3% NO, less than 1.5% O_2 ; the balance is N_2

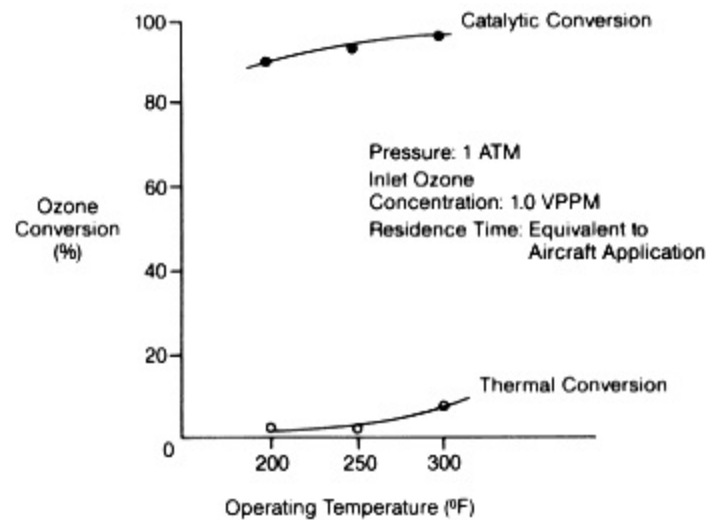


Fig. 6
Comparison of thermal versus catalytic conversion of ozone.

[207]. The NO is produced by reaction of N_2 and O_2 , at cylinder temperatures in excess of $1,500^\circ\text{C}$. Some NO_x is also produced from bound nitrogen compounds present in fuel and/or oil.

Early there was hope that nonprecious metal catalysts, such as CuO , Cr_2O_3 , NiO , FeO , and CoO , would be successful as catalysts in abating these pollutants. However, poisoning by oxides of sulfur, produced by oxidation of sulfur compounds present in gasoline, led to severe permanent catalyst deactivation [208, 209]. Other undesirable reactions between the carrier and these oxides [210], as well as oxidation and reduction reactions [211], also contributed to the ultimate elimination of base metal catalysts from consideration for this application.

Application of precious metal-containing catalysts for oxidizing emissions from off-the-road vehicles began as early as 1960. This provided the basis for new catalyst formulations for the automobile application (Fig. 7). The specific details of composition and method of manufacture remain proprietary; however, most automobile exhaust catalysts contained a 2:1 or 3:1 ratio of Pt to Pd [212] on high surface area Al_2O_3 [213, 214], with promoters and stabilizers also present. The total precious metal content varied from about 0.05% for pellets to 0.10.15% for ceramic honeycomb monoliths. In 1985, over 1 million troy ounces of precious metal was used for emission control. This represents the single largest use of precious metals in industrial catalysis.

Precious metal-containing catalysts were used because they were more resistant to sulfur oxide poisoning and could be formulated to resist thermal degradation more so than base metal oxides. However, Pb present in tetraethyl lead, used as an octane booster, was a selective poison that would react with the precious metal, form a compound or alloy, and cause a

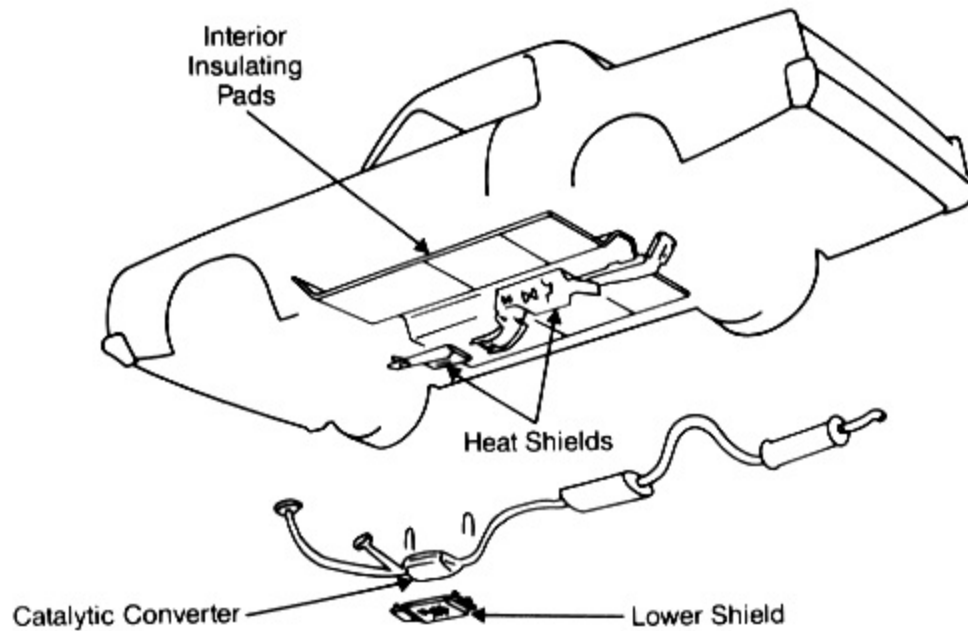


Fig. 7

Physical location of the automatic exhaust catalyst.

decrease in catalytic efficiency. It has also been suggested that deposition of Pb increases diffusional resistance [215], also resulting in a decline in performance.

Because of this, and its health hazard, it became necessary to remove the lead from the gasoline and improve octane by additional reforming or by blending other octane-boosting components to the fuel. It is for this reason that automobiles equipped with converters require lead-free gasoline.

Two distinct types of exhaust train catalytic systems were developed. Some automobile manufacturers utilized a pelleted catalyst bed (Fig. 8A) of Pt and Pd deposited on particulate carriers of γ -alumina; others pursued a relatively new design using a magnesium alumina silicate ceramic monolith or honeycomb support (Fig. 8B) upon which the precious metal-containing γ -alumina was deposited on the walls of each channel [216]. Each design has its virtues. For example, particulate beds offered large amounts of catalyst per volume resulting in low temperatures to initiate oxidation of the pollutants. However, the bed must be shallow and wide to minimize pressure drop, which necessitates a large canister to contain the catalyst. Furthermore, a special spring-loaded container had to be made to secure the pellets to prevent attrition by vibration and subsequent fluidization. Honeycomb systems, with 300400 cells in.², eliminated pressure drop problems and had configurational advantages of higher geometric surface areas than particulate catalysts. However, additional manufacturing steps

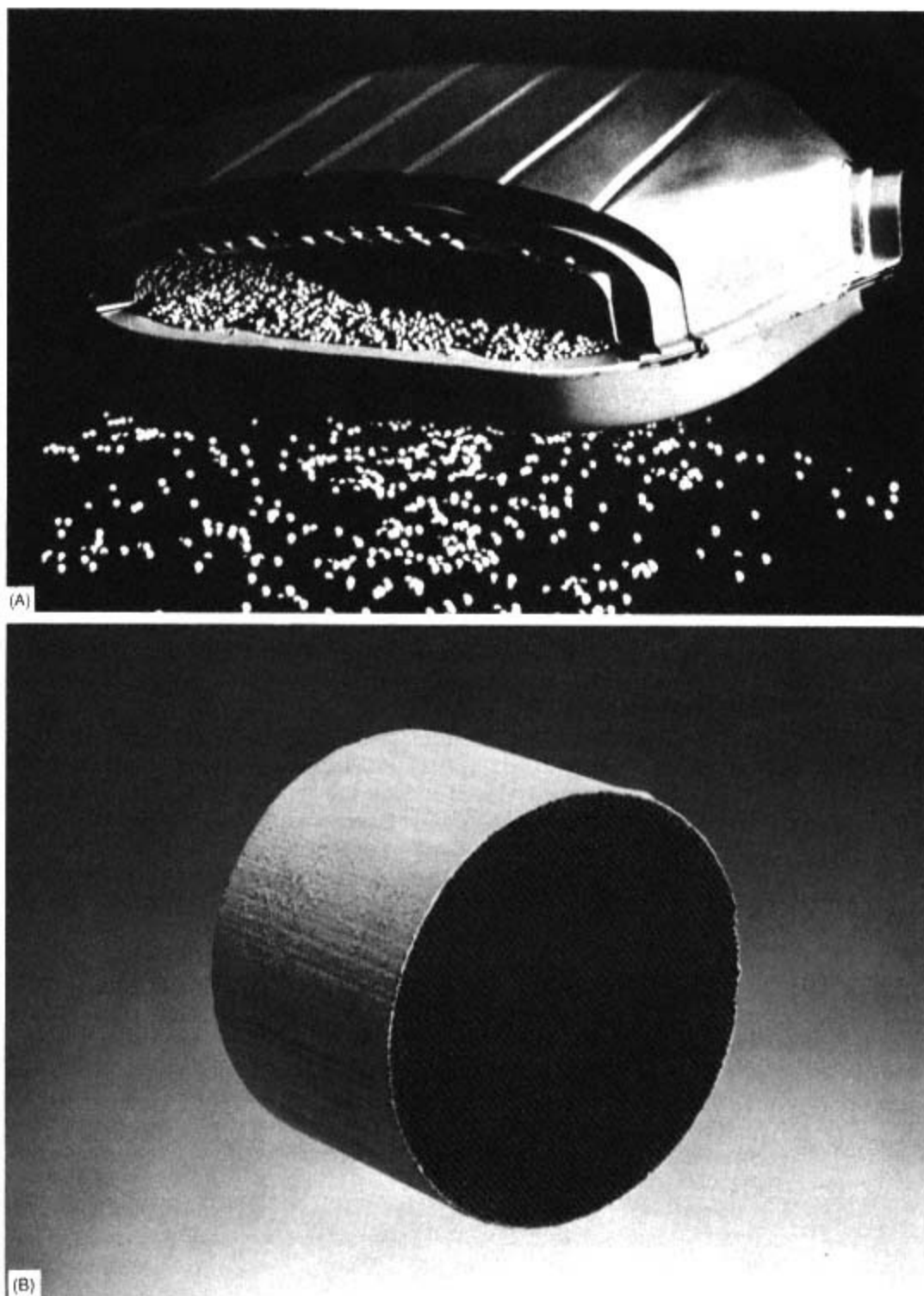
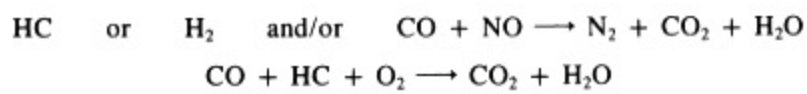


Fig. 8
Automobile catalytic converter:
(A) beaded bed; (B) monolith.

were required to deposit an adherent high surface area γ -alumina-catalyzed "washcoat" to the walls of the monolithic channels. Automobile manufacturers developed fully satisfactory systems, implemented first in 1975, so both approaches were used; however, today the monolithic ceramic honeycomb appears more favorable. Honeycombs made of metal are also finding some use in special applications.

Following successful implementation of catalysts for controlling CO and HC emissions, the reduction of NO_x emissions to less than 1.0 g/mile had to be addressed. The reduction of NO to N₂ requires a reducing environment; CO and HC required excess air. Exhaust emanating from the engine was sufficiently reducing so that an NO reduction catalyst (i.e., Ru) could be used in the first bed while air pumped into a second catalytic bed oxidized the CO and HC. The net reactions involved reduction of NO by CO, HC, or H₂ present in the exhaust followed by oxidation of the remaining CO and HC:



However, ruthenium formed volatile oxides whenever the catalyst was exposed to an oxidizing environment [217]. If Pt and Pd catalysts were used in the first bed, some of the NO was reduced to NH₃, which was reoxidized in the second bed to NO.

This dual-bed concept was replaced with a system capable of catalytically converting all three pollutants when the air-fuel ratio was maintained close to stoichiometric. The development of the O₂ sensor in Europe allowed this system concept to advance. This sensor, present in the exhaust, monitors O₂ content. Any significant fluctuation in O₂ concentration changes the voltage in the sensor, which in turn feeds back to the fuel feed system to maintain the air-fuel ratio. In this manner, the catalyst operates in a narrow air-fuel "window" near the stoichiometric point. A single bed then functions as a three-way conversion catalyst (TWC) [216], converting all three pollutants simultaneously as shown in Fig. 9. The first TWC-equipped vehicles were introduced in model year 1978 by Volvo.

Although the precise catalyst compositions and methods of preparation are proprietary, most are comprised of a mixture of Pt and Rh in a 5:1 weight ratio (total metal about 0.1%) on high surface area stabilized γ -alumina as a pellet or washcoat on a monolith.

Promoters, such as NiO, CeO₂, and Fe₂O₃, are also used as oxygen storage components [216, 218]. Theory suggests that during fuel-to-air perturbations, some oxygen from these reducible oxides is made available to oxidize the CO and HC.

Under normal driving conditions the catalyst operates around 400-600°C; conversions close to 100% are obtained. Normal operating space velocities vary from 10,000 to 100,000 h⁻¹.

Under cold-start conditions, the catalyst is insufficiently active to convert pollutants and

hence the minimum temperature for "light off" is of

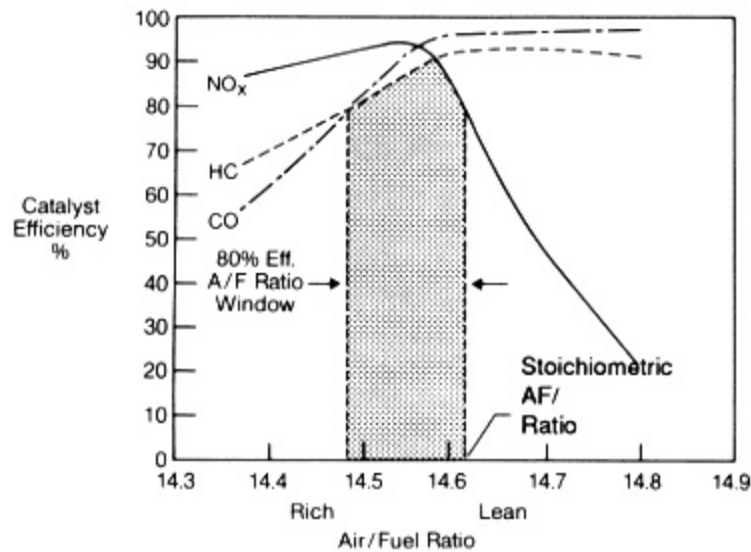


Fig. 9
Efficiency of simultaneous catalytic conversion of CO, HC, and NO_x, versus air/fuel ratio.

major importance, since the emission standards include a cold start as part of the federal testing cycle. There is a continuing effort on the part of catalyst suppliers to lower the light off temperature.

The catalyst must continue to function efficiently throughout a wide range of driving conditions. Rapid accelerations, misfiring, and poor engine conditions can lead to extremely high concentrations of pollutants and oxygen in the converter, and consequently, thermal resistance against the exotherms generated by these conditions must be built into the catalyst. Because these conditions are relatively common in the lifetime of an exhaust catalyst (50,000 miles by U.S. law), deactivation by high-temperature excursions is one of the major problems experienced [215, 219]. Under temperature conditions of 1,000–1,100°C the precious metals undergo agglomeration or sintering [220], and the high surface area support converts to a low-area structure (i.e., α -alumina), decreasing the available catalytic surface area and activity of the catalyst. Taking this into account, catalyst suppliers have developed formulations resistant to these thermal stresses.

Catalyst deactivation is also caused by poisoning. Traces of Pb present in the fuel can react with the precious metal components and cause deactivation. In addition, phosphorus, and zinc from lubricating oils, can form undesirable compounds and glazes on the catalyst surface, which increases diffusional resistance, impeding performance [221]. Other deactivation mechanisms, including undesirable reactions between the precious metals and the support [219] and sulfur and heavy metal (i.e., Ba) poisoning [215,

222], are critical and are considered in the formulation of the catalyst [223].

Regeneration methods have been suggested [224]; however, none have been put in practice.

Organic Abatement

In manufacturing most consumer products, at least one processing step involves the use of organic compounds that ultimately become components of plant effluent. These volatile organic compounds (VOC) may be solvents serving as carriers for active agents, unreacted feedstock, or decomposition products. As a result, actual composition and types of material vary with the processes, such as those listed here [225]:

Paint bake ovens: ketones, toluene, xylene

Metal-coating operations: ketones, toluene, xylene

Wire-enameling operations: phenols, xylenols, and methylated benzene

Chemical plants: formaldehyde, phthalic anhydride, acrylonitrile

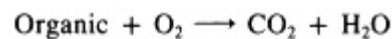
Printing: toluene, n-hexane, ethyl acetate, propanol

Textile plants: alcohols, phenol, toluene

Electronic plants: cellulose acetate butyrate and paraffins

Because the concentration of VOC in the air is usually low, noncatalytic thermal incineration has an economic disadvantage since substantial amounts of additional fuel must be added to combust the VOC.

Since catalytic reactions occur at temperatures between 300 and 400°C and thermal incineration occurs at temperatures close to 700 or 800°C, catalytic removal is often the choice for abatement. The catalyst removes the volatile organics by catalytic oxidation [226] by the generalized reaction



Operating temperatures of a catalytic reactor depend on a number of variables; one of the most important is organic composition. Figure 10 shows typical performance of a catalyst for conversion of various organic solvents. Highly oxygenated materials can usually be combusted at lower temperatures than saturated hydrocarbons.

Monolithic materials, either ceramic or metal, are becoming most favorable as supports upon which a catalyzed washcoat is deposited, although various other catalyst structures, such as particulates or screens, are used. Catalyst compositions are proprietary; however, most commonly, 0.3% Pt on high surface area alumina either as a particulate or washcoat on a monolith is used. In limited cases, small amounts of Rh are added to promote the Pt [226, 227].

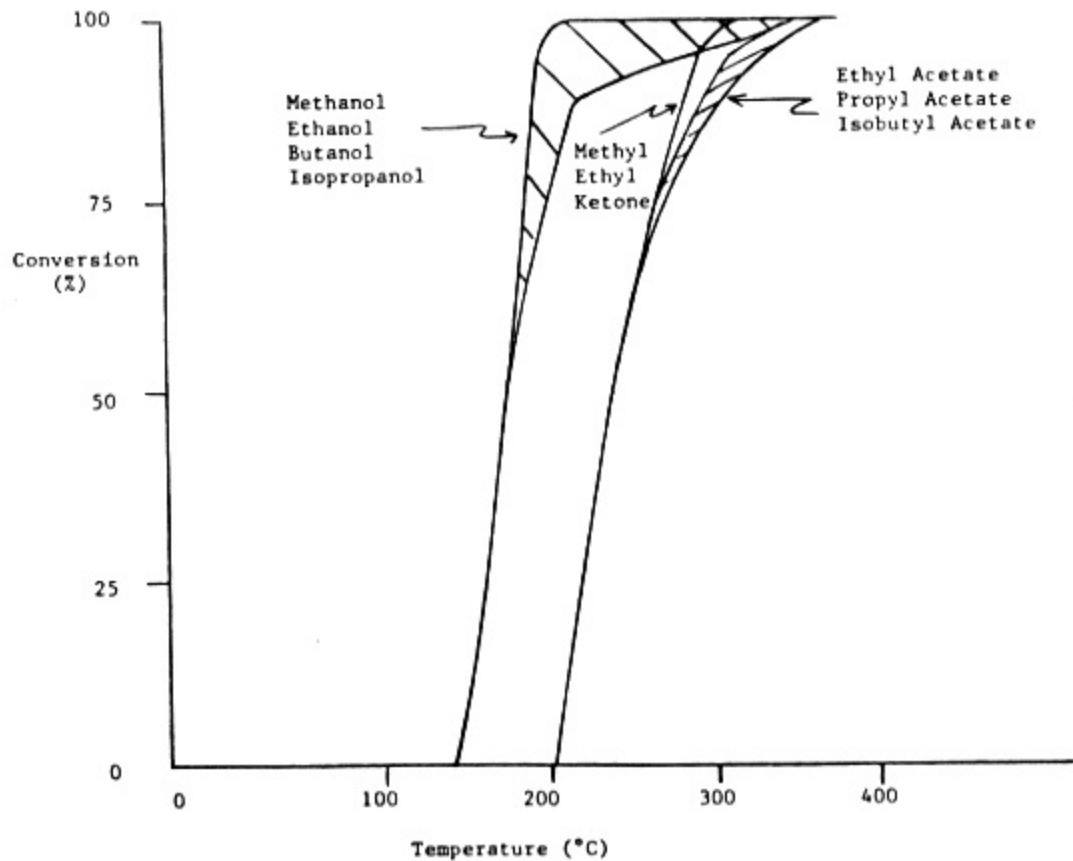


Fig. 10
Catalytic abatement of various organic solvents.

Fixed-bed vapor-phase reactors that operate from 30,000 to 60,000 h⁻¹, depending on the abatement required (e.g. 99 versus 90%), are used in the exhaust vents of the plant (Fig. 11).

Deposition of particulate dust on the catalyst surface is a common cause of catalyst deactivation. In organic abatement systems [228, 229], noncombustible, solid material deposits "mask" the catalyst surface. Iron oxides from the corrosion of upstream ductwork, metal oxides, such as SiO₂, from the processing of silicone materials, and organic chars are frequently found on the catalyst. Catalyst suppliers have developed special chemical treatments to remove these impurities and thus can restore the activity almost to its initial fresh value. These regenerating solution compositions are proprietary; however, mild acids, bases, and chelating solutions are used [228]. Proper reactor operation and periodic maintenance by chemical cleaning of the honeycomb catalyst result in these catalytic systems operating from 5 to 10 years.

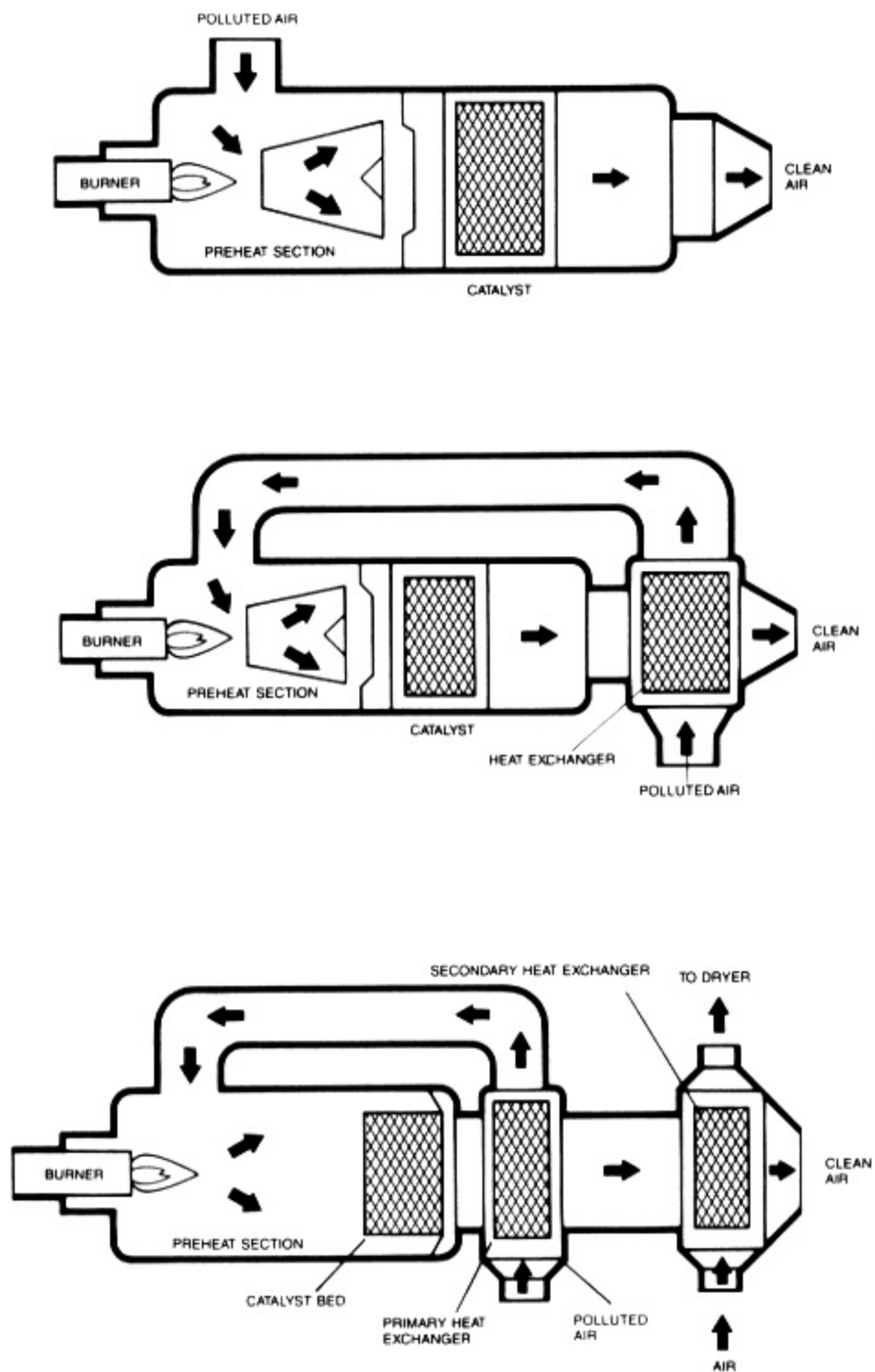
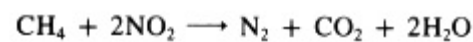


Fig. 11
Hydrocarbon abatement systems.

Nitric Oxide Abatement

Nitric oxide emissions are produced during the manufacture of nitric acid. Reddish brown NO₂ is emitted to the atmosphere in the presence of large excesses of air. Since the environment is oxidizing and NO₂ must be reduced to N₂, it is necessary in nonselective catalytic reduction (NSCR), to first consume all the excess O₂ by combustion with added fuel, such as CH₄ (natural gas). The NO₂ is then catalytically reduced to N₂ by the residual fuel, that is, CH₄. The reactions are

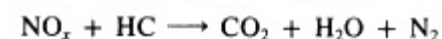
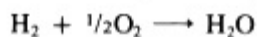
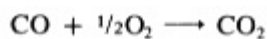


Platinum and rhodium supported on a high surface area alumina as a particulate or a washcoat on a honeycomb structure are the most often used catalysts [226, 230]. A fixed-bed vapor-phase reactor is used, operating at 50,000–100,000 h⁻¹ space velocity.

Deactivation usually occurs because of thermal sintering of the precious metal and/or Al₂O₃ after continuous exposure to temperatures close to 900°C. Deposition of iron from upstream corrosion of piping can also deactivate the catalyst.

Recent air pollution regulations have resulted in the use of catalysts on stationary engines to abate both CO and NO_x [231]. For applications in which engine exhaust is oxygen deficient, less than 1 % excess O₂ (richburn engine), nonselective catalytic reduction technology is used.

Uncontrolled emissions from a rich-burn engine result in 13% CO, and 1,000–3,000 vppm NO_x in the engine exhaust. Operation of a Pt-Rh-containing catalyst, on the rich side, results in reduction of NO_x in the discrete simplified sequential reaction steps



The first series of reactions remove the oxygen; the second series converts the NO_x into nitrogen. Using an oxygen sensor in the exhaust, the engine is adjusted to operate rich of stoichiometric, thereby permitting these reactions to occur. Figure 12 shows the emissions as a function of the air-fuel ratio.

Performance of the catalytic system can be designed and operated to produce less than 2,000 vppm CO and less than 100 vppm NO_x in the

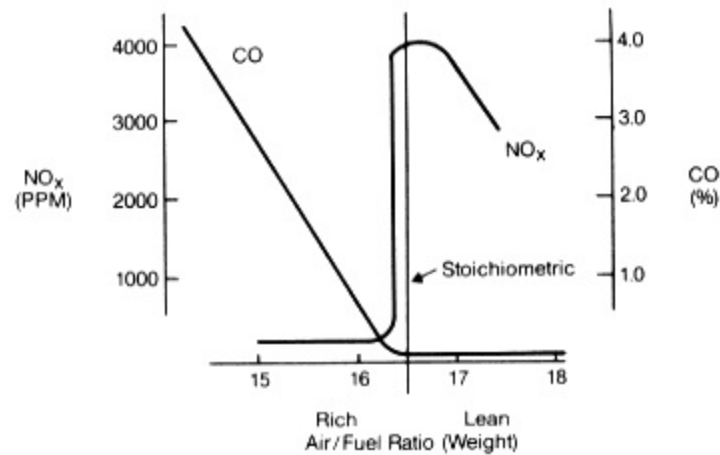


Fig. 12

Catalytic conversion of NO_x and CO versus air/fuel ratio for a natural gas-fueled engine.

engine exhaust [225, 232], with design space velocities ranging from 50,000 to 100,000 h⁻¹.

Selective catalytic reduction utilizes NH₃ to selectively reduce NO or NO₂ in the presence of large amounts of air. In the late 1950s, a supported Pt catalyst was successfully used, provided the temperature was maintained in a narrow range of 180–220°C [233, 234]. Above this range, NH₃ was rapidly oxidized to NO. More recently, since 1977, new technology based on V₂O₅ supported on TiO₂ has supplanted Pt catalyst technology.

Carbon Monoxide Abatement from Gas Turbines

NO_x emissions from gas turbines can be reduced by decreasing the flame temperature in the combustor by water injection. This is common practice for gas turbines utilizing a wide variety of fuels, including natural gas and fuel oil. Lower flame temperatures result in higher CO emissions, however, and thus abatement is necessary. With conversions of 80–95%, levels of 100–200 ppm are common using a monolith (100–200 cells per in.², ceramic or metal) washcoated with high surface area alumina upon which Pt is dispersed. This catalyst operates between 315 and 600°C, with space velocities from 100,000 to 200,000 h⁻¹ depending on required CO conversion. Because of the high throughputs, up to 400 lb/s, the catalyst is subjected to severe mechanical disturbances and must be housed to protect it from vibration and shock. A catalyst module may measure 2 × 2 ft; as many as 200 of these can be present in turbine ducts as large as 30 ft wide × 400 ft high.

Catalyst deactivation from sintering is slow but most often occurs because of fouling from ductwork material and/or physical deterioration from excessive vibration.

Off-the-Road Vehicles

Even before it became mandatory for automobile exhaust catalysts, liquid propane-, gasoline- [235], and diesel- [236, 237] powered vehicles, which operated in confined spaces, were equipped with catalysts to combust CO and hydrocarbon emissions. Hydrocarbon-fueled forklift trucks operating in poorly ventilated environments were a primary application for such systems.

In this application, a Pt-based catalyst, usually in the form of a honeycomb, is fitted in the exhaust system of the vehicle so that air mixes with the pollutant-laden exhaust. The mixture is passed through the catalytic bed, where the CO is converted to CO₂ and unburned hydrocarbons converted to CO₂ and H₂O. It should be noted that no significant NO_x is produced in these types of vehicles.

For these vehicles, the temperature of operation varies depending on any given duty cycle; 500-600°C is normal, although abatement is initiated at less than 200°C. Design space velocities can vary from 100,000 to 200,000 h⁻¹. Conversion efficiencies vary with the fuel and duty cycle of the truck; however, over 99% CO is removed and up to 90% of the hydrocarbon [237].

Catalyst deactivation is slow and is usually associated with poisons present in the fuel.

Wood Stoves

Wood stoves (Fig. 13) operate normally in a deficiency of air to maintain a slow burn of the wood. For this reason, stoves are very airtight, permitting only a controlled amount to enter the primary combustion chamber. Consequently, incomplete combustion generates large concentrations of CO and partially oxidized hydrocarbons. Distillable organics, such as creosotes, released when the wood is heated, condense in the chimney and are the cause of "chimney fires."

Combustion of these products would increase the overall wood stove efficiency, improve safety, and clean up the emissions. Thus, energy and environmental factors led to development of a new stove design that incorporates a ceramic monolithic honeycomb (16 cells/in.²) catalyst [238]. Products of the primary wood combustion are admixed with secondary air and passed through a low cell density metallic [239] or ceramic structure coated with Pt and Pd on high surface area alumina. Carbon monoxide and organic materials are then catalytically combusted, providing heat efficiency improvements of 15 % and a cleaner effluent with reported creosote removals of 85-95% and CO removal of 90% at space velocities of 10,000-20,000 h⁻¹ [240]. The design incorporates a catalyst safety bypass that prevents backup of gases into the room in the event that the monolithic catalyst becomes blocked.

Temperature in the monolithic catalyst naturally depends on the heat of combustion of the pollutants; however, the system is designed to handle about 1,000°C. Thermal

sintering of both precious metals and γ -alumina is

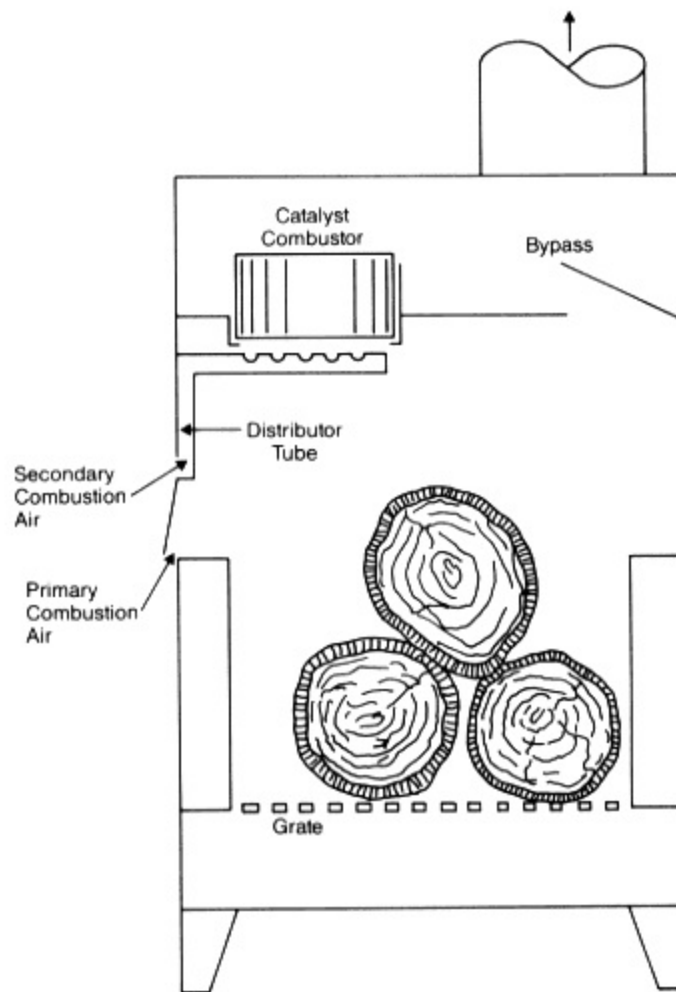


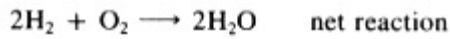
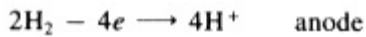
Fig. 13
Wood-burning stove equipped with a monolithic catalyst.

a major source of deactivation, although impurities from the wood or other fuels can shorten catalyst life by poisoning.

Electrocatalysis

Fuel Cells

Electricity can be generated with a high degree of efficiency by electrocatalytically oxidizing H_2 and reducing O_2 in a fuel cell. The major advantage of a fuel cell is that it directly converts chemical into electrical energy [241]. The electrochemical reactions for an acid electrolyte fuel cell are



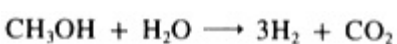
Conventional power plants combust fossil fuels to generate heat to turn the turbine blades in a magnetic field. This introduces a mechanical step, limiting the overall efficiency by the Carnot cycle. Since a fuel cell bypasses the mechanical step, it is as much as 60% more efficient than a conventional power generating plant. Furthermore, if heat generated during the electrochemical reactions is utilized (i.e., cogeneration), efficiencies close to 90% (based on H₂ utilized) can be achieved.

Electrocatalysts are critical to achieve optimum conversion of the H₂ and O₂. In this application, the catalyst of choice for the anodic H₂ oxidation reaction is 10% Pt on conductive carbon [242]. The electrocatalyst is prepared on a conductive fibrous material. It is laid on a conductive, nonporous grooved carbon plate, grooved to permit H₂ distribution through the electrocatalyst. This is shown in Fig. 14.

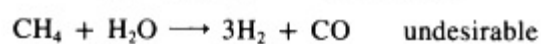
When an anode must function in a liquid electrolyte, such as phosphoric acid, and a gas rich in H₂, contacting the gas with the active Pt sites requires penetration through the liquid acid layer. For this reason, a wetproofing agent, such as Teflon, is added to the catalyst formulation to avoid flooding the electrode and to allow adequate H₂ gas-anode contact.

The cathodic reaction of O₂ reduction (O₂ from air) is more difficult kinetically [243] than the anode reaction and lowers the overall power output to approximately 60% of the theoretical maximum. The best cathode catalyst is 10% Pt, promoted with other metals or metal oxides, supported on graphitic carbon [242]. This inert support is necessary to minimize corrosion from the reaction of the O₂ with the carbon. The electrode preparation and its arrangement in the cell is similar to that of the anode. The anode and cathode are separated by a solid matrix saturated with phosphoric acid, the electrolyte (see Fig. 14).

A fuel cell system is composed of a fuel processor that converts a hydrogen-rich molecule, such as methanol or natural gas, to H₂ by catalytic steam reforming.



or



The electrochemical cell, which also includes the Pt anode and cathode, phosphoric acid electrolyte, and a power conditioner that converts d.c. to a.c. current, is shown as a block diagram in Fig. 15.

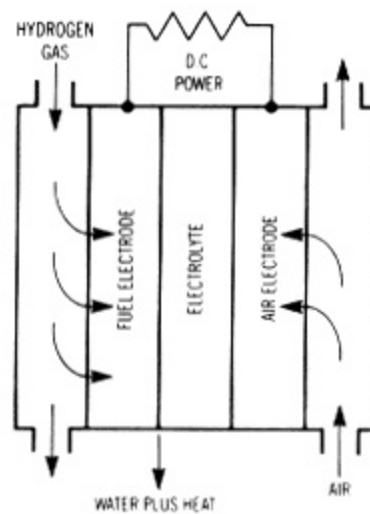
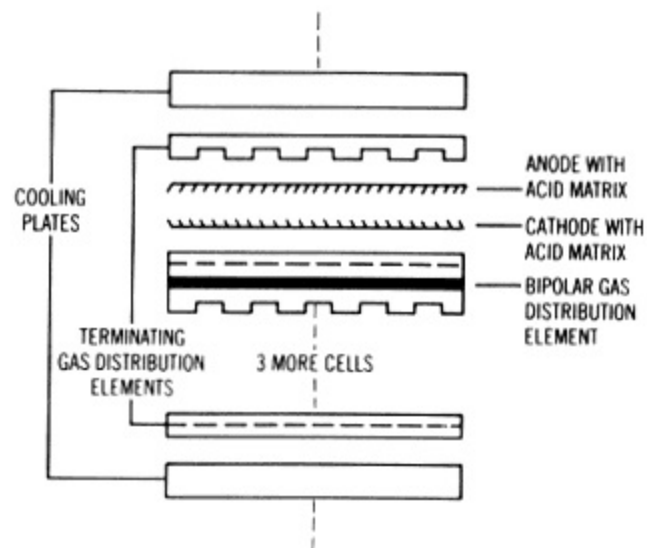


Fig. 14
Phosphoric acid fuel cell stack:
(top) four cells in series;
(bottom) basic fuel cell.

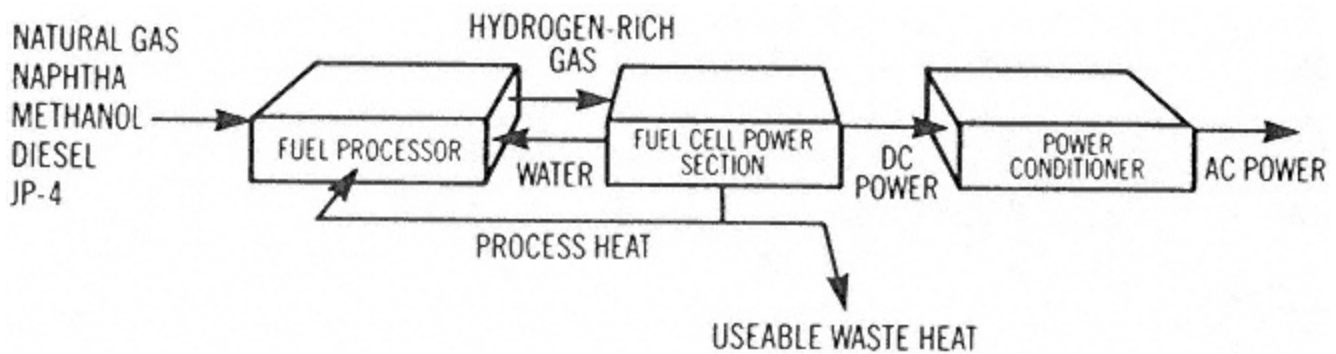


Fig. 15
Integrated fuel cell power plant.

The total power output of each cell is approximately 150200 A/ft² and 0.7 V. It can be increased by stacking the electrochemical cells in series so that the opposite side of the plate upon which the anode is placed is used for the cathode of the adjacent cell. In this manner, each side of the nonporous conductive plate functions as a gas distribution manifold for anode and cathode (see Fig. 14). To maintain the operating temperature around 200°C, cooling plates are integrated every five or six cells into the final system.

The anode catalyst is exposed to increasing amounts of CO (~0.52%) present in H₂ fuel. The CO results from incomplete steam reforming (thermodynamic limitation). Its percentage increases to a maximum of approximately 2 % as the H₂ is electrocatalytically oxidized and inhibits the anode reaction by strong chemisorption.

Sintering and possibly dissolution of the Pt cathode in the acid electrolyte are considered among the major sources of deactivation. At fuel cell conditions, these processes are relatively slow and a catalyst typically lasts many thousands of hours.

Although acid fuel cells for power generation are still not commercial, demonstration programs exist [244, 245]. Solid polymer electrolyte (SPE) fuel cells [246, 247] are available for operation on pure H₂ fuels and temperatures not exceeding 100°C.

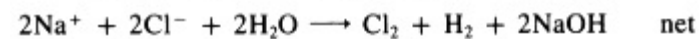
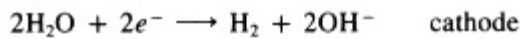
Alkaline fuel cells were used on the space shuttle Columbia, but because of their extreme sensitivity to CO₂ they have found little use in terrestrial applications. Active programs are being conducted in Europe using Pt electrocatalysts.

Chlor-Alkali Cells

One of the major industrial applications for ruthenium is as an electrocatalyst for the anodic oxidation of chloride ion in the production of Cl₂. Ruthenium oxide is deposited on a sheet of expanded titanium mesh and oxidized to produce a solid solution film of RuO₂/TiO₂ on the base Ti metal [248]. This dimensionally stable anode (DSA) replaced graphite, which was subject to considerable corrosion during use. The presence of the

electrocatalytic RuO₂ enhances the activity, is more stable, improves the overall life of the anode, and produces a purer product relative to graphite.

The cathodic reactions are similarly of great industrial importance since H₂ and NaOH are produced. The cathode material was frequently mercury but is now being replaced by mild steel. The overall reactions are:



The anode and cathode are separated by an asbestos diaphragm or, more recently, a cation-exchange resin membrane. A number of commercial processes exist [249, 250].

Hypochlorite Generation

Bacterial-laden waters that would normally foul a ship's seawater system can be treated by the addition of Cl₂ [251] as an oxidizing agent. For these and other applications, such as oil well drilling or water treatment plants, it is more convenient to generate the Cl₂ electrochemically on site from seawater as opposed to shipping Cl₂ to the site or storing it on board. Devices have been developed [252, 253] that electrolytically decompose seawater, resulting in the generation of dilute solutions of Cl₂ in water. The electrocatalytic reaction leads to the generation of Cl₂ at a Pt-coated titanium anode and OH⁻ and H₂ at the steel (or titanium) cathode. The Cl₂ reacts with the alkali, forming hypochlorite according to the reaction



Typically, concentric pipes are configured with one coated with Pt to form an electrocatalytic anode. The NaCl-containing seawater passes through the pipe, where Cl₂ is generated at the anode and H₂ and NaOH at the cathode. The system typically operates at 150 psig and 90°C. The hypochlorite solution is then pumped to the specific location for reaction with microorganisms. The major source of deactivation is due to fouling from minerals present in the seawater.

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Chlorination, Liquid Phase and Vapor Phase

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General

Chlorination has been defined as a unit process in which one or more chlorine atoms are incorporated into a chemical compound. The compound may be an aliphatic, an aromatic, or others. In a broader sense, the term chlorination is applicable to all reactions and processes in which chlorinated compounds are produced.

Generally, this chemical change causes the density, viscosity, and chemical reactivity of the chlorinated organics to increase. On the other hand, the specific heat, dielectric constant, solubility in water, and flammability are usually decreased [37, 84]. The chemical properties of chlorinated hydrocarbons are determined largely by the hydrocarbon group from which they are derived [156]. The chlorinated hydrocarbons are all covalent compounds. They are soluble in organics but virtually insoluble in water. These and other changes in physical and chemical properties lead to many uses of chlorocompounds. The physical and thermodynamic properties of chlorinated compounds are available in many standard references. Comprehensive correlations of vapor pressure, heat of vaporization, heat capacity, density, viscosity, surface tension, thermal conductivity, and second virial coefficients of a number of chlorinated aliphatics and aromatics have been made [5457, 147, 167]. Those for chlorine and hydrogen chloride have also been compiled [131, 166].

The uses of chlorination products are numerous. To name a few examples, chloromethanes are useful solvents, vinyl chloride is used in plastics, ethyl chloride is used for the manufacture of automotive antiknocks, and many chlorinated aromatics are excellent insecticides, herbicides, and fungicides. Perhaps the most important use of chlorocompounds is its function as a raw material for hundreds of other useful chemicals. The versatility of chlorocompounds may be appreciated by looking at the range of compounds an alkyl chloride can be converted to as shown in Fig. 1 [138].

Alkyl chloride can also react with alkali-metal cyanides to form nitriles, with sulfites to form water-soluble sulfonates, with alkoxides to form ethers, with mercaptides to form thioethers, with anhydrous sodium acetate to form esters, and with magnesium to form Grignard reagents which are useful intermediates in organic synthesis [156]. This list can go on and on.

Chlorinated compounds represent one of the most important branches of chemistry. They number in the hundreds and are found in almost all groups and families of organic chemicals. Scores of these are of commercial and industrial importance. Ethylene

dichloride and vinyl chloride, for example, are among the

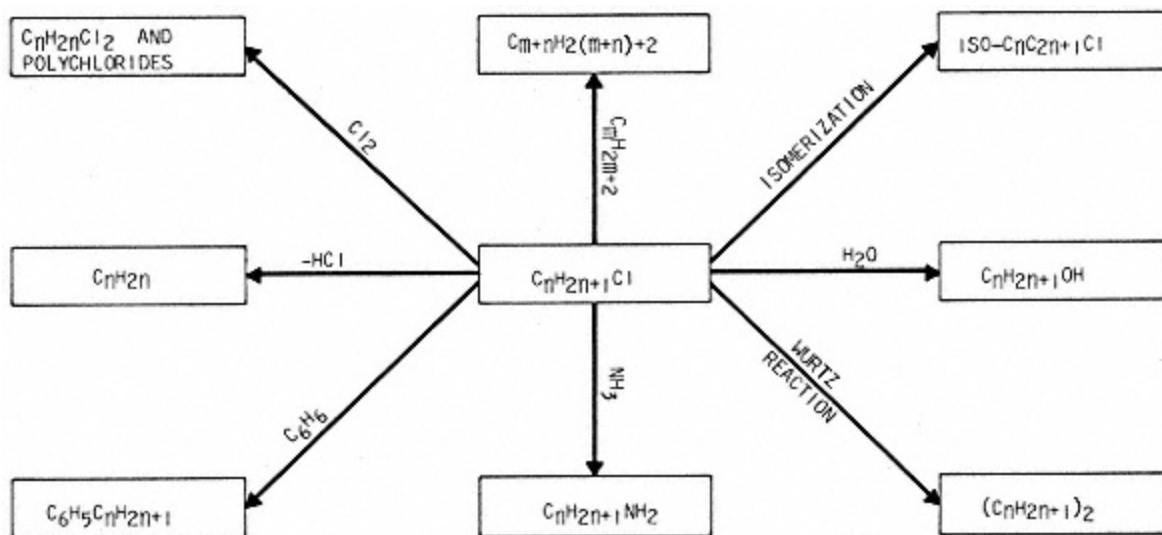


Fig. 1.
Some reactions of alkyl chlorides.

largest volume chemicals. These and others with high tonnage production are listed along with their sales and unit price figures in Table 1 [150153].

It is evident from Table 1 that, while the production rate of several chlorinated compounds fluctuates with time, for most of these it is on the increase. The year-to-year increases in chlorine consumption, the majority of which is used for chlorinating chemicals, are impressive and are available elsewhere in this handbook.

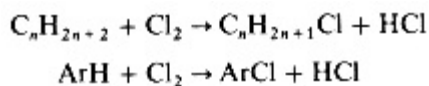
Types of Chlorination

Chlorination of organic compounds can be effected in a number of ways. The reaction can be carried out in the vapor phase or in the liquid phase. The chlorinating agent includes chlorine, hydrogen chloride, and numerous organic and inorganic chlorides, such as SO_2Cl_2 , PCl_5 , and tert-butyl hypochloride. Heat, light, and/or catalyst are generally used to promote the reaction. Among the common catalysts employed are: ferric and cupric salts; bromine; iodine; the halides of antimony, tin, arsenic, phosphorus, aluminum, and sulfur; and activated carbon and clays [64]. To promote chlorination photochemically, mercury lamps are often utilized. These lamps provide a light wavelength in the range of 3000 to 5000 Å which is absorbed by chlorine molecules. Thermal chlorination is carried out in the vapor phase, usually at temperatures above 250°C. The thermal means is most widely used, as it is cheap and simple. The use of gamma radiation and electric arc to initiate chlorination has also been reported [50, 163].

The literature abounds in the theory and practice of chlorination. One way of summarizing the vast amount of pertinent information is to classify the material by the reaction mechanism and the chlorinating agent used as follows.

Substitutive Chlorination

One of the most common ways of chlorinating a compound involves the substitution of an atom or a group of atoms (e.g., functional groups) by chlorine. In the case of a paraffin or an aromatic, a hydrogen atom is substituted by a chlorine atom:



Substitution of a second hydrogen or all the available hydrogen in the hydrocarbon is not only feasible but often occurs.

Discovered in mid-nineteenth century, substitutive chlorination of paraffins has been studied extensively and practiced commercially since the early 1930s. A number of generalizations about this reaction can be made. Notably, the conclusions reached by Haas and co-workers have withstood the test of time and have become established rules on chlorination.

Their observations and those of other investigators are listed as follows [67, 68, 72, 99]:

No carbon skeletal rearrangement takes place if pyrolytic conditions are avoided [67, 139].

Substitutive chlorination has poor selectivity; every monochloride possible is formed. At a given temperature, the vapor-phase reaction is somewhat more selective than that carried out in the liquid phase. Moisture, light, and carbon surfaces all do not affect selectivity [68, 139].

The ease or the rate of substituting hydrogen in a given hydrocarbon is tertiary > secondary > primary [68, 139].

In vapor-phase chlorination, the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution.

The rate of substitutive chlorination of saturated hydrocarbons is greater than that for unsaturated hydrocarbons [64].

For vapor-phase chlorination of saturated hydrocarbons, high reaction pressure favors substitution of primary hydrogen over secondary hydrogen [64].

Reaction temperature has only a minor effect on selectivity. Typically, a decrease of 50°C in the chlorination temperature results in a selectivity increase of about 10% [99], as the activation energies of propagation between primary and secondary CH bonds, or between secondary and tertiary CH bonds are usually less than 0.5 kcal. The trend is that the higher the temperature, the more random is the substitution [37, 68]. An unexpected observation has been reported, however. For pentane through decane, the relative selectivity of secondary to primary hydrogen substitution passes through a minimum at about 250°C, and begins to increase above that temperature [72].

Other conditions being equal, a high mole ratio of hydrocarbon to chlorine favors monochloride over polychloride formation [38]. In fact, for light paraffins, the ratio of monochlorine/polychloride formation is linearly proportional to the mole ratio of hydrocarbon to chlorine [64].

The stability of chlorinated hydrocarbons relative to pyrolysis is in the order primary > secondary > tertiary.

The material of construction of the reactor and the condition of the reactor surface affect the reaction rate [16].

The following observations apply to liquid-phase chlorination:

Product distribution is a complicated function of temperature and interphase mass transfer in the chlorination of long-chain paraffins such as n-dodecane [120].

For alkylbenzenes, high temperatures (120 to 130°C) promote substitution in the side chain, while low temperatures (e.g., 30 to 50°C) and the use of catalyst (e.g., ferric chloride or aluminum chloride) favor the replacement of nuclear hydrogen [64].

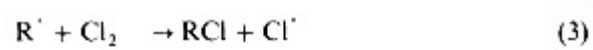
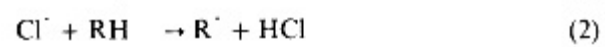
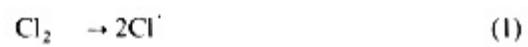
Aliphatic solvents have little effect on selectivity. However, aromatic solvents and those with polarizable atoms such as carbon disulfide can have positive effects.

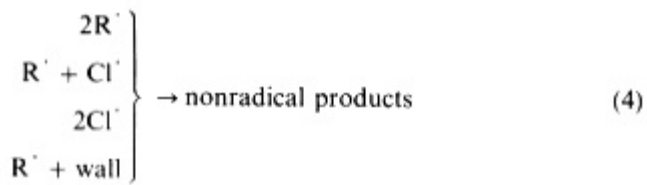
Substitutive chlorination is exothermic; the heat release is about 24 kcal/mol for each hydrogen atom substituted [38]. Some typical heats of reaction are as follows [64]:

	kg·cal/g-mol halogen
$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$	-24.3
$\text{CH}_4 + 2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + 2\text{HCl}$	-24.0
$\text{CH}_3\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{HCl}$	-23.7
$\text{CH}_4 + 3\text{Cl}_2 \rightarrow \text{CHCl}_3 + 3\text{HCl}$	-24.0
$\text{CH}_4 + 4\text{Cl}_2 \rightarrow \text{CCl}_4 + 4\text{HCl}$	-24.1
$\text{C}_2\text{H}_6 + 6\text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6 + 6\text{HCl}$	-24.9
$\text{C}_6\text{H}_{14} + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_{13}\text{Cl} + \text{HCl}$	-33.4
$\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$	-31.4
$\text{C}_6\text{H}_5\text{Cl} + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{HCl}$	-29.7
$\text{C}_6\text{H}_4\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_3\text{Cl}_3 + \text{HCl}$	-29.3
$\text{C}_6\text{H}_3\text{Cl}_3 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_2\text{Cl}_4 + \text{HCl}$	-27.5

Additional thermodynamic data are available elsewhere [8, 34, 86, 89, 99, 126]. The change in entropy is small, and the equilibrium is in favor of the right-hand side of the reactions at all temperatures [64].

The mechanism of substitutive chlorination, which has been the source of much dispute, is now generally regarded as involving the following steps [35, 72, 116, 138]:





The reverse reactions of Eqs. (2) and (3) are probably of relatively little importance [15]. The termination reaction on the wall, as may be expected, is more dominant in small reactors than in large ones in which the surface-to-volume ratio is lower [17].

Reaction (1) is the initiation step. The formation of the chlorine radical can be brought about photochemically, thermally, or catalytically [8]. Beta and gamma radiation have also been demonstrated as an effective means of promoting the chlorination reaction [38, 72].

Reactions (2) and (3) constitute the chain propagation step in which a chlorine free radical is first consumed and then regenerated. The chain length can be quite high of the order of 10^3 to 10^7 . In other words, for every radical generated by the initiation step, some 10^3 to 10^7 molecules of reaction product can be formed [72]. This range of high values means that the reaction can be conducted with very low levels of radical initiation.

Of these two chain propagation reactions, the attack of the hydrocarbon by the chlorine radical has been theorized to be rate limiting [104]. However, based on kinetic evidence, others believe that the rate-limiting step depends on the nature of the hydrocarbon [133]. Still others argue that rates of these two steps must be essentially equal [15]. Apparently, conclusive evidence supporting any one stand is lacking.

The chain termination step is represented by Reactions (4). The wall of the reaction vessel and the impurities in the reaction mixture such as oxygen are often thought to promote chain termination [106].

The above reaction mechanism applies to both vapor- and liquid-phase processes [72].

This free radical chain mechanism was substantiated by considering the bond dissociation energies and the activation energy barrier [99]. The bases for this calculation are (1) the entropy changes are small and nearly constant for similar reactions, and (2) the most stable compounds are formed at the most rapid rates. Another supportive evidence is that the reaction can be accelerated by radical-producing catalysts such as tetraethyl lead and hexaphenyl ethane and inhibited by radical scavengers such as oxygen [72].

The kinetics of substitutive chlorination has been studied by many investigators [35, 99, 115]. Considerable disagreement exists in the literature concerning the proper form of the kinetic equation [15]. Reportedly, the difficulty stems from poor reproducibility of experimental results. Using hydrogen as a model for alkane and aromatic hydrocarbons, Bernstein [15] proposed the following rate equation:

$$\frac{d[\text{HCl}]}{dt} = k[\text{H}_2][\text{Cl}_2]^{0.5}$$

where

$$\log_e k = 30.3 + (-34,200/RT)$$

For photochemical, vapor-phase chlorination of propane, the reaction rate was found to increase to the second order of chlorine concentration and to the first order with respect to light intensity [23].

For liquid-phase chlorination of n-dodecane, the reaction rate was found to depend on the first order of the paraffin concentration and zero order of the chlorine concentration [119]. The dependence on light intensity was approximately half order. That is,

$$\frac{d[\text{RCl}]}{dt} = k[\text{RH}][\text{I}]^{0.5}$$

Similar kinetics was obtained in the beta radiation-induced, liquid-phase, side-chain chlorination of toluene. In this case the reaction rate also varied with the square root of radiation intensity [165]. For these heterogeneous chlorination reactions involving gaseous chlorine and liquid hydrocarbon, mass transfer limitations have a significant effect on product distribution [120, 121, 156].

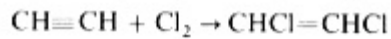
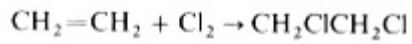
Liquid-phase chlorination of stearic acid initiated by benzoyl peroxide was found to be similar to that of paraffins from a mechanistic standpoint [106]. Kinetically, the reaction occurs first order for chlorine and approximately first order for benzoyl peroxide.

Silberstein [134] studied the kinetics of benzene chlorination catalyzed by stannic chloride. He postulated a reaction mechanism in which the reaction between stannic chloride and a π -complex of chlorine and benzene is the ratecontrolling step. Both homogeneous liquid-phase experiments and vaporliquid heterogeneous experiments were carried out. The kinetics for the homogeneous liquid reaction is first order in free (uncomplexed) benzene, free (uncomplexed) chlorine, and stannic chloride. Under heterogeneous conditions, where chlorine is bubbled through the liquid phase containing benzene and catalyst, diffusional limitations restrict the rate of reaction, but the selectivity or product distribution is not affected.

In industrial practice, substitutive chlorination is carried out in both liquid and vapor phases. In vapor-phase reaction, initiation by thermal means is most widely used for simplicity and economy [98]. On the other hand, liquid-phase chlorination reactions are generally initiated catalytically or photochemically [8]. All three methods of initiation are used commercially, and each has its advantages and disadvantages. With the photochemical method, traces of impurities can inhibit chlorination through chain termination. On the other hand, by-products such as unsaturated compounds, tar, and carbon are not formed. The thermal method requires high temperature, which together with the large heats of reaction, demands close temperature control. The advantages of the thermal method are high capacity, low installation cost, no inhibitor effect, and complete chlorine reaction [70].

Additive Chlorination

In additive chlorination a chlorine molecule is added to an unsaturated (olefinic or acetylenic) bond resulting in a dichloride. Some typical examples are the formation of ethylene dichloride and acetylene dichloride:



As in substitutive chlorination, molecular chlorine is the chlorinating agent. For this reason, substitutive and additive chlorinations are often called direct chlorination.

Some general remarks about the characteristics of additive chlorination are as follows:

Compared to substitutive chlorination, additive chlorination is relatively easy and proceeds at low, such as ambient, temperatures [9].

Additive chlorination is highly specific and the chlorine atoms are symmetrically distributed.

The vapor-phase reaction of olefin and chlorine yields both substitutive and additive chlorinations [107]. The relative importance of each depends on the operating conditions. High temperature favors hydrogen abstraction (or substitutive chlorination); increasing the chlorine-to-olefin ratio in feed has the opposite effect.

More often than not, additive chlorination is carried out in the liquid phase.

Lewis acids such as FeCl_3 , ZnCl_2 , and PCl_3 are often employed to catalyze the reaction. These catalysts are chlorine carriers in the sense that they can add on and give up chlorine during chlorination, as they are capable of existing at two valence states [64].

Additive chlorination of olefins is exothermic. That of acetylenes is even more so [38]. The changes in enthalpy content for some typical reactions are as follows (using 25°C, 1 atm, and gaseous reactants and products as reference):

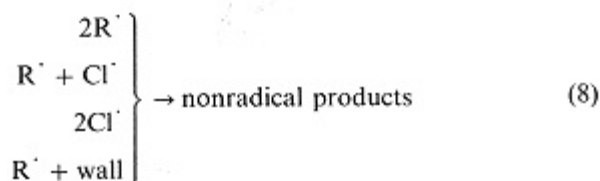
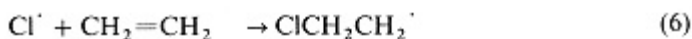
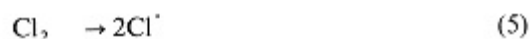
	kg·cal/g-mol halogen
$\text{C}_2\text{H}_4 + \text{Cl}_2 \rightarrow \text{CH}_2\text{ClCH}_2\text{Cl}$	-43.8
$\text{C}_2\text{H}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_4$	-37.8
$\text{C}_2\text{HCl}_3 + \text{Cl}_2 \rightarrow \text{C}_2\text{HCl}_5$	-34.0
$\text{C}_2\text{Cl}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6$	-32.0

The change in entropy is generally about -20 cal/mol per degree. The equilibrium, therefore, is in favor of the right-hand side of the reactions at all temperatures up to

about 1000°C [64]. Additional thermodynamic data are available elsewhere [86].

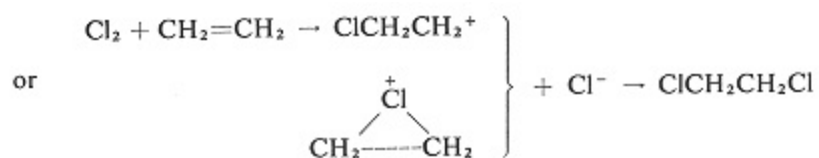
Both a free radical reaction mechanism and a polar mechanism have been postulated for additive chlorination.

The free radical reaction mechanism is generally thought to proceed as follows, using the chlorination of ethylene as an example [116]:



The breakdown of a chlorine molecule to form two chlorine radicals in Reaction (5) can be accomplished either thermally or photochemically. Reactions (6) and (7) constitute the free radical chain with the formation of ethylene dichloride as the product.

The polar reaction pathway which is widely accepted may be shown as follows [116]:



By this mechanism, the chlorine-chlorine bond is broken heterolytically and both the α -chlorocarbonium ion structure and the bridged chloronium ion structure are thought to be the reaction intermediates.

Conclusive evidence for defining the reaction mechanism is lacking. Difficulties in obtaining good experimental reproducibility have been reported. Apparently, the effects of surface, moisture, light catalysis, and even the structure and the concentration of olefin are contributing factors. It is possible that both polar and radical reaction mechanisms can occur at the same time [116].

Kinetic studies of additive chlorination are not numerous. Some fundamental data have been compiled [35, 83, 115]. Vapor-phase photochlorination of olefins and chloroethylenes showed that the rate of chlorination is half order with respect to light intensity and first order with respect to chlorine [40, 72]. The concentration effects of olefins and chloroethylenes showed up only under low pressures (less than 70 mmHg).

An investigation of liquid-phase chlorination of acetylene [45], catalyzed by either antimony pentachloride or ferric chloride, showed that the reaction is first order with respect to the hydrocarbon and that the rate-controlling step is the mass transfer of acetylene in tetrachloroethane which is the reaction

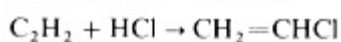
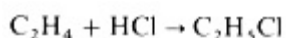
product and a solvent for chlorine and catalyst. A significant conclusion is that, for the ranges of variables investigated, the reaction rate is not dependent on catalyst concentration nor temperature.

For liquid-phase chlorination of ethylene, the development of a steady-state reaction model and the elucidation of the effects of mass transfer, reactor design, and operating condition are the subject of a three-part paper [36]. It was found that the multistep reaction is mass transfer controlled. A bubble column reactor offers no advantage over a continuous stirred tank reactor. The most important parameter affecting the product distribution and ethylene conversion is the ethylene and chlorine feed ratio. Generally, a high ethylene-to-chlorine mole ratio (such as 3 or 4:1) favors the formation of ethylene dichloride and 1,1,2-trichloroethane, accompanied by low conversion (around 20 to 30%). A low ethylene-to-chlorine mole ratio (1:1 or less) results in a high ethylene conversion (60 to 70%) and a high proportion of tetra- and pentachloroethanes. The control of batch reactors for additive chlorination of ethylene has been investigated [105].

Hydrochlorination; Dehydrochlorination

Hydrochlorination is the addition of hydrogen chloride across an unsaturated bond. Dehydrochlorination is the removal of hydrogen chloride or its equivalent from a chlorocompound resulting in an unsaturated bond.

Examples of hydrochlorination are the production of ethyl chloride from ethylene and vinyl chloride from acetylene as represented by



The importance of the latter reaction is evident from the fact that, up until several years ago, about 30% of all acetylene manufactured in the United States was used in the production of vinyl chloride [2].

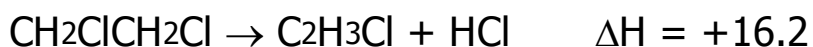
Hydrochlorination can be carried out in both vapor and liquid phases [84]. The vapor-phase reactions are usually effected under high pressure. Those in the liquid phase are catalyzed by heavy metal chlorides such as mercuric chloride and aluminum chloride [2, 9]. Both an ionic mechanism and a free radical chain mechanism have been postulated for this reaction [52, 139]. For gas-phase hydrochlorination of acetylene, a kinetic model [60] and an analysis of the operation of industrial reactors [87] have been reported.

Producing few by-products, hydrochlorination is generally quite selective. Only one chlorine atom is introduced at each addition [139]. Following Markownikov's rule, the stereochemistry favors the addition of chlorine atom to the carbon carrying the least number of hydrogen atoms [84].

The replacement of an alcohol group by chlorine from HCl is often also called hydrochlorination [37]. Examples of this are the conversion of methanol and ethanol to

methyl chloride and ethyl chloride, respectively. Using a catalyst such as ZnCl_2 , this type of process has excellent selectivity (90 to 98% yield).

kg·cal/g-mol halogen

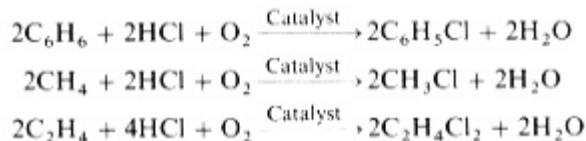


Additional thermodynamic data are available elsewhere [89].

Thermodynamic calculations show that these dehydrochlorinations are favorable at temperatures above 250°C.

Oxychlorination

One type of chlorination which has gained much attention in recent years and which competes with direct (additive and substitutive) chlorination is oxychlorination, sometimes also called oxidative chlorination. The process makes use of hydrogen chloride as a source of chlorine along with oxygen (or air) and a catalyst. Several significant applications of oxychlorination include the production of monochlorobenzene, chloromethane, and, in greatest quantity, dichloroethane (or ethylene dichloride), a raw material for vinyl chloride manufacture. Using these compounds as examples, the following overall equations can be written:



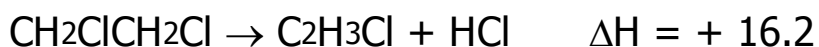
Strictly speaking, a process in which hydrogen chloride and oxygen are used for chlorination should be called oxyhydrochlorination, and that in which chlorine and oxygen are used should be called oxychlorination. However, the distinction is seldom made and both are called oxychlorination.

Oxychlorination is not new. Its first commercially successful application was in the Raschig process for converting benzene to chlorobenzene and ultimately to phenol [85]. The basic features of the process were developed at the works of Dr. F. Raschig, GmbH, Ludwigshaven, Germany in 1929-1935 by Dr. Walter Prahl [66]. Oxychlorination was carried out in the vapor phase at 290°C using a copper chloride catalyst suspended on an inert support. While this process has enjoyed much recognition, its popularity has decreased over the years. The reasons are the relatively high capital investment required and the high utility load (steam and gas or oil). Finding suitable materials of construction to contain corrosive mixtures of hot steam, chlorine, and hydrogen chloride is another major difficulty [85]. Another objection is that the process is limited to compounds which are stable against oxidation under oxychlorination conditions.

The history and the fundamental aspects of oxychlorination have been described by Allen

and Clark [5]. Included in their review paper are descriptions of oxychlorination catalysts, reaction kinetics, and thermodynamics of component reactions.

kg·cal/g-mol halogen



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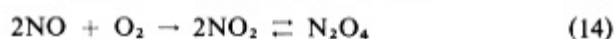
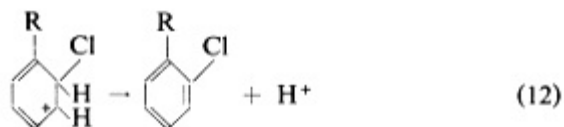
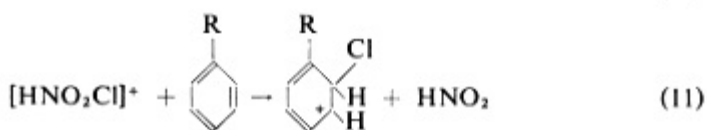
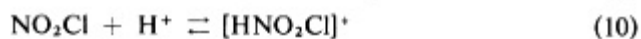
and Clark [5]. Included in their review paper are descriptions of oxychlorination catalysts, reaction kinetics, and thermodynamics of component reactions.

In recent years, with the supply of HCl exceeding its demand and the cost of HCl much less than chlorine, the application of oxychlorination for making chlorinated compounds has increased. Many oxychlorination processes have been developed and commercialized. For illustrative purposes, two of the recent ones, the Gulf oxychlorination process and Lummus' Transcat Process, will be described.

Unlike the Raschig process, the Gulf process oxychlorinates aromatic compounds in the liquid phase [129]. Because of the lower temperatures associated with the liquid-phase reaction, a wide range of organic compounds which are not otherwise stable against oxidation can be chlorinated. Thus mono- and polychloro derivatives of benzene, toluene, xylenes, biphenyl, ethylbenzene, and naphthalene as well as other aromatic hydrocarbons, paraffins, and fatty carboxylic acids can all be made according to Gulf literature.

The reaction makes use of dilute hydrochloric acid, oxygen (or air), and nitric acid as catalyst. Typical operating conditions are 80 to 130°C and 700 to 1200 kPa. In the case of benzene, a 80% conversion and a 95% selectivity (of mono- to dichlorobenzene) are claimed. These conversion and selectivity levels are higher than those reported for vapor-phase oxychlorination [130].

The postulated reaction mechanism for the process entails the following set of equations:

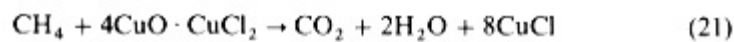
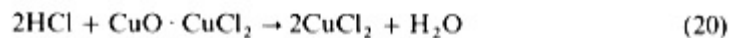
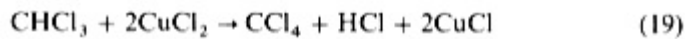
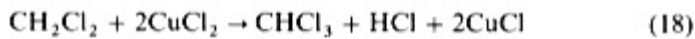
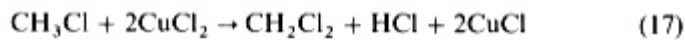
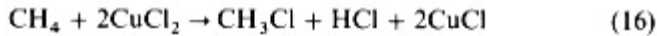


Nitric acid and hydrochloric acid react to form nitryl chloride (Eq. 9) which is protonated (Eq. 10) under acidic environment. The protonated nitryl chloride, in turn, reacts with the aromatic compound, producing nitrous acid as a byproduct (Eqs. 11 and 12). The mechanism for the oxidation of nitrous acid to nitric acid is represented by Eqs. (13) through (15) which are well known.

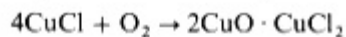
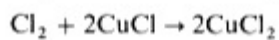
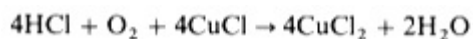
Another oxychlorination process is the Transcat technology licensed by Lummus for the synthesis of chloromethane, dichloroethane, vinyl chloride, and other C₂ chlorinated hydrocarbons [30]. The process makes use of a molten salt catalyst system consisting of cupric chloride and cuprous chloride. Two

reactors, one for chlorination and the other for catalyst regeneration, are used. In the chlorination, molten cupric chloride functions as the chlorinating agent and is reduced to cuprous chloride. Along with chlorinated hydrocarbons, hydrogen chloride is produced as a by-product. Both cuprous chloride and hydrogen chloride are fed to an oxidation reactor where the former is converted back to cupric chloride.

The reactions which occur in the chlorinator include the following, using methane as an example:



Yield loss through methane oxidation is shown in Eq. (21). Another source of yield loss is from the pyrolysis of chlorinated compounds. The cupric oxychloride shown in Eq. (20) and (21) is produced during the catalyst reoxidation step which consists of the following reactions:



In a typical case, methane is contacted with a molten catalyst system comprised of cupric chloride, cupric oxychloride, and HCl at 370 to 500°C and 1 to 5 atm. The contact time is of the order of 10 to 15 s. Methane conversion ranges from 13 to 30%, but can be as high as 95%. Selectivity to chloromethanes is around 80 to 90%, and substantial flexibility in the product mix can be achieved.

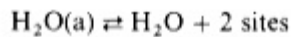
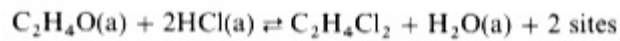
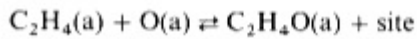
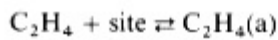
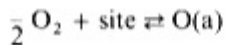
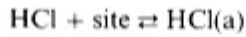
The advantages claimed for this process include: (1) Chlorine can be supplied in the form of molecular chlorine, hydrogen chloride, or waste chlorocarbons; (2) no undesirable by-products or objectionable wastes are discharged; (3) high operational safety as oxygen is supplied to the hydrocarbons in chemical combination rather than by direct contact; and (4) waste chlorocarbons and mixtures of hydrocarbons can be processed [30]. These advantages contribute toward low raw material and manufacturing costs.

Other oxychlorination processes have also been developed and commercialized [3, 6, 38, 140]. Most are catalyzed by copper chloride, a modified Deacon-process catalyst. The support material for the catalyst is of considerable importance as evidenced by the number of patents on it. Potassium chloride or other alkali metal chlorides are generally added to the catalyst to

lower its melting point. Thus, at operating conditions, most oxychlorination catalysts apparently contain a liquid phase [4].

Kinetic studies of oxychlorination of methane [7], ethylene [21], and monochlorobenzene [6] have been reported. The last two studies both rejected the classical Deacon reaction mechanism in which chlorination of the organic compound is postulated to take place between the adsorbed chlorine and the adsorbed organic molecule. Instead, the experimental data support the occurrence of an oxidation step prior to the chlorination.

For ethylene, an ethylene oxidation mechanism was proposed as follows [21]:



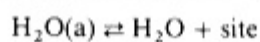
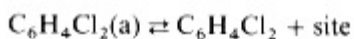
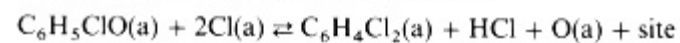
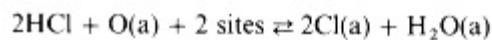
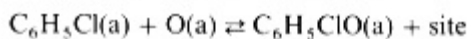
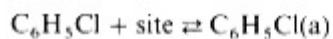
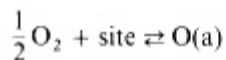
The resultant Hougen-Watson type rate equation, with the rate expressed as moles of dichloroethane per liter-second and partial pressure in millimeters of Hg, is

$$\text{Rate} = \frac{6.83 \times 10^{-7} (p_{\text{C}_2\text{H}_4}) (p_{\text{O}_2})^{1/2}}{[1 + 0.0017 (p_{\text{C}_2\text{H}_4}) + 0.0355 (p_{\text{O}_2})^{1/2} + 0.0165 (p_{\text{H}_2\text{O}})]^2}$$

The energy of activation is 24.5 kcal/mol. The power series correlation, obtained with a nonlinear regression program, is

$$\text{Rate} = 2.49 \times 10^{-6} (p_{\text{C}_2\text{H}_4})^{0.73} (p_{\text{O}_2})^{0.34} (p_{\text{H}_2\text{O}})^{-0.18}$$

For monochlorobenzene, the following reaction mechanism fits the experimental data [6]:



The reaction rate expression with units of moles of dichlorobenzene (CB) per hour per cubic centimeter is

$$\text{Rate} = \frac{0.609 (p_{\text{CB}})(p_{\text{O}_2})^{1/2}}{[1 + 0.0454 (p_{\text{CB}}) + 0.4413 (p_{\text{O}_2})^{1/2}]^2}$$

or, in power law form:

$$\text{Rate} = 0.491 (p_{\text{CB}})^{0.531} (p_{\text{O}_2})^{0.151} (p_{\text{HCl}})^{0.038}$$

Thus these two studies indicate that the oxychlorination rate depends largely on the partial pressures of the organic feed and oxygen.

On the other hand, for Kellogg's liquid-phase oxychlorination of ethylene in homogeneous aqueous copper chloride solutions, the rate of 1,2-dichloroethane formation is found to be dependent only on catalyst concentrations [140] as follows:

$$\text{Rate} = 0.0269[\text{CuCl}][\text{CuCl}_2 - 2\text{CuCl}]^2$$

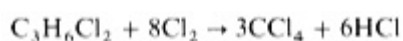
where rate is in units of moles product per liter per hour. The energy of activation is 22 kcal/mol.

All in all, oxychlorination has the net effect of combining two steps in one process: it converts HCl to a chlorinating agent which in turn chlorinates the hydrocarbon. As such, it is in competition with processes such as Kellogg's Kelchlor Process [78] which converts hydrogen chloride to chlorine. The primary disadvantage of oxychlorination is that, compared to direct chlorination, more expensive materials of construction and therefore a higher capital investment are required.

Chlorinolysis

Chlorinolysis, a term coined by Hass and his students in 1941, is a method for producing simple perchlorocarbons, e.g., carbon tetrachloride, perchloroethylene, and hexachloropropane [66, 156]. It involves the breakage of a carbon-carbon bond when a hydrocarbon or a chlorinated hydrocarbon is reacted with excess chlorine at a high temperature (400 to 700°C). Fully chlorinated hydrocarbons with fewer carbon atoms than the starting material are obtained. Thus the term "perchlorination" is a synonym and is often used instead.

An example of chlorinolysis is that of 1,2-dichloropropane for the production of carbon tetrachloride:



At 600 to 700°C, perchloroethylene is also formed from the following equilibrium:



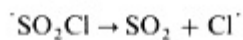
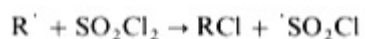
By recycling either carbon tetrachloride or perchloroethylene, the relative production of these products can be adjusted [109]. Thus 1,2-dichloropropane, an excess by-product from the propylene oxide process employing the chlorohydrin route, can be profitably converted to useful products [85].

Chlorination by Miscellaneous Agents

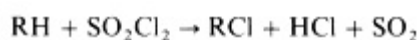
In addition to chlorine and hydrogen chloride, other agents have been used to effect chlorination of organic compounds. They include sulfuryl chloride (SO_2Cl_2), thionyl chloride (SOCl_2) [92], tert-butyl hypochlorite (BuOCl) [124, 144], tert-butyl chloride (BuCl) [159], chlorine monoxide (Cl_2O) [146], trichloromethane sulfonyl chloride ($\text{CCl}_3\text{SO}_2\text{Cl}$), trichloromethane sulfenyl chloride (CCl_3SCl), N-chlorosuccinimide (NCS), phosphorus pentachloride (PCl_5) [114], ferric chloride (FeCl_3), antimony chlorides, phosgene (COCl_2), iodobenzene dichloride ($\text{C}_6\text{H}_5\text{ICl}_2$), and cupric chloride (CuCl_2). For economic reasons, the use of these reagents is less common than Cl_2 and HCl , and is generally invoked for convenience in laboratory synthesis or when specific selectivity is desired. Their availability, optimum reaction conditions, and other pertinent information are summarized in Table 2 [99]. Additional comments follow.

Sulfuryl Chloride (SO_2Cl_2). Used primarily for its ease of handling, sulfuryl chloride is often selected for chlorinating saturated and unsaturated hydrocarbons. Two significant advantages of this chlorinating agent are: (1) Heat release is low, for much of the heat of chlorination is absorbed by the dissociation of sulfuryl chloride; and (2) the gaseous by-product formed, HCl and SO_2 , are easily removed.

The reaction is promoted by light, heat, metallic chlorides, activated carbon, and peroxides, and is inhibited by oxygen. A free radical mechanism, viz.,

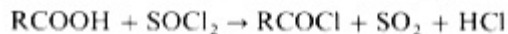
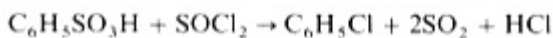
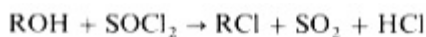


has been postulated, giving the overall reaction



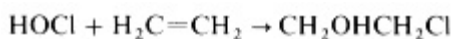
The selectivity of sulfuryl chloride for chlorination is somewhat better than that of chlorine.

Thionyl Chloride (SOCl_2). With thionyl chloride, chlorine can replace various groups such as OH , SH , NO_2 , SO_2H , hydrogen, and oxygen in a compound. Some of its applications are [64]



The preparation of acid chlorides, as in the last reaction above, is perhaps most common since thionyl chloride seldom attacks aldehyde, ketone, or ethoxy groups.

Hypochlorites. Hypochlorites in acidic and alkaline solutions are effective chlorinating agents. The reaction of ethylene and hypochlorous acid at 20 to 30°C and 2.5 atm produces ethylene chlorohydrin [64]:



Ethylene dichloride is often formed as a by-product.

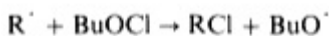
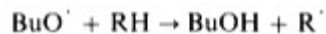
Alkali hypochlorite solutions can readily chlorinate nitroparaffins, as in the production of chlorpicrin (trichloronitromethane):



Depending on the relative amount of hypochlorite solutions used, mono-, di-, and trichloro derivatives can be obtained [64].

As a chlorinating agent, tert-butyl hypochlorite offers several unique advantages, namely, no acidic by-products are formed, almost any CH bond will be attacked, and allylic chlorination can be selectively effected. Many examples of its application can be cited [20, 22, 123, 161, 162]. tert-Butyl hypochlorite can be prepared simply by passing chlorine into an aqueous mixture of tert-butyl alcohol and sodium hydroxide. It can also be prepared in an acidic medium such as acetic acid.

In general, the chlorination is initiated photochemically. Allylic chlorination of butenes and pentenes are carried out at -78 to 100°C. Conversion of toluene to benzyl chloride (84% yield) can be effected at 0°C or below. A chain free-radical mechanism has been postulated with the following propagation steps:



Trichloromethanesulfonyl Chloride. For substitutive chlorination of n-alkanes, trichloromethanesulfonyl chloride clearly offers better selectivity than chlorine, sulfuryl chloride, or BuOCl. However, for compounds which give rather stable radicals, such as cumene and cyclohexane, the reagent is inefficient. A chain reaction mechanism similar to that for sulfuryl chloride has been proposed:

TABLE 2 Comparison of Chlorinating Agents^a

Reagent	Availability	Optimum Reaction Conditions	Selectivity ^b	By-products	Synthetic Comparison
Cl ₂	Readily available; inexpensive	Photochemical initiation with excess substrate or inert solvent (CCl ₄) as medium; wide temperature range possible	Least of all reagents (t:s:p ≈ 4:2.5:1 at 25°C)	HCl: gaseous and easily removed but acidic	Cheapest reagent and most selective
Cl ₂ in C ₆ H ₆ or CS ₂	Solvents readily available	As for Cl ₂ except for solvent	Considerable increase over Cl ₂ (t:s:p ≈ 50:100:10:1)	HCl: solvent must be removed and should have bp different from expected product	Simplest method to achieve high selectivity
SO ₂ Cl ₂	Commercially available	Benzoyl peroxide initiator at 80 to 100°C; a high-boiling cosolvent desirable for low-boiling substrates	Variable, but small, enhancement over Cl ₂ , probably dependent on SO ₂ concentration; same as Cl ₂ in presence of aromatic solvent or substrates	HCl and SO ₂ : both gaseous	Easier to measure on a small scale than gaseous chlorine (true for all reagents here also); less prone to competitive polar reactions; not enough to have particular utility as a criterion
BuOCl	Commercially available; easily synthesized; relatively stable	As for Cl ₂	Moderate (t:s:p ≈ 44:8:1 at 40°C); comparable to Cl ₂ in complexing solvents	tert-Butyl alcohol: nonacidic; bp close to common solvents facilitates removal	Selectivity comparable to Cl ₂ in complexing solvents without a product; will attack almost any reagent of choice for allylic chlorination
CCl ₃ SO ₂ Cl	Commercially available; more expensive than CCl ₃ SOCl	Benzoyl peroxide initiation preferable to photoinitiation	High (s:p ≈ 2530:1); increased relative reactivity compared to chlorine at sites leading to	HCl, SO ₂ , and CHCl ₃ ; bp of latter comparable to that of common solvents	Good reagent to achieve maximum selectivity between CH bonds of moderate to high reactivity

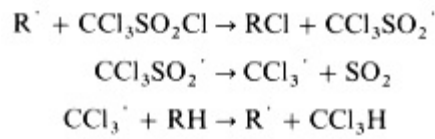
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Reagent	Availability	Optimum Reaction Conditions	Selectivity ^b	By-products	Synthetic Comparison
			resonance-stabilized radicals		inefficient for compounds giving stable radicals
CCl ₃ SCl	Commercially available	Photoinitiation; rather wide temperature range	High (t:s:p \approx 100:30:1 at 0°C); comparable to CCl ₃ SO ₂ Cl	HCl and CCl ₃ SSCCl ₃ ; latter can be reconverted to starting material but must be isolated and may interfere with workup	Seems to offer little advantage over CCl ₃ SO ₂ Cl except cost, but gives complex by-products
N-Chlorosuccinimide	Commercially available	Benzoyl peroxide initiation in CCl ₄ at 80 to 100°C	Very similar or identical to Cl ₂	Succinimide; largely insoluble in CCl ₄	No increased selectivity but more efficient than Cl ₂ ; not generally used
R ₂ NH + NCl	Easily synthesized from amine and tert-BuOCl or N-chlorosuccinimide	Acetic acid-sulfuric acid solvent; Fe ²⁺ or photoinitiation	Probably quite large s:p ratio; most strongly dependent on deactivation by electron-withdrawing groups	Amine (R ₂ NH): large volume of acid must be handled during workup	No obvious advantage for hydrocarbon chlorination but may offer advantages over Cl ₂ for functionalizing sites of molecules from electron-withdrawing substituents
PCl ₅	Commercially available	Benzoyl peroxide initiation at 80 to 100°C	High s:p ratio; aliphatic:benzylic ratio comparable to Cl ₂	HCl + PCl ₃ ; latter rather noxious and may interfere during workup	No obvious advantage over Cl ₂
C ₆ H ₅ ICl ₂	Easily synthesized from C ₆ H ₅ I and Cl ₂	Photoinitiation in CCl ₄ or CHCl ₃	High (t:s:p \approx 350:20:1)	HCl + C ₆ H ₅ I plus minor products of side reactions; C ₆ H ₅ I may be recycled but may interfere during workup	Probably little advantage for hydrocarbon chlorination over CCl ₃ SO ₂ Cl; may be generated for forming unrearranged dichlorides of highly branched olefins that give complex products with Cl ₂

^aFrom Huyser [72] with permission of Marcel Dekker, Inc.

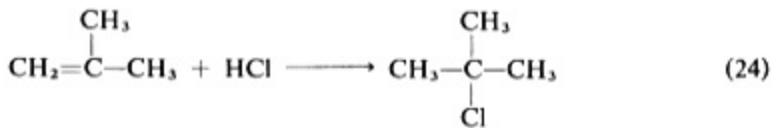
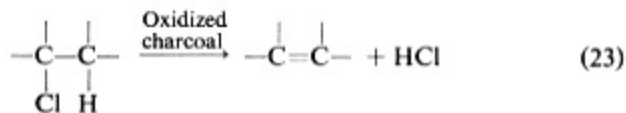
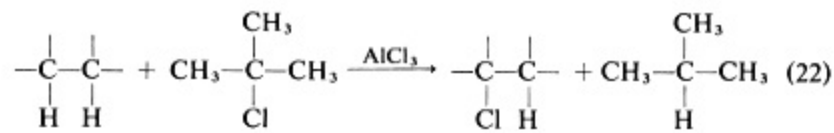
^bThe ratios are based on chlorination of small molecules such as n-butene and 2,3-dimethylbutane [99]. t = tertiary hydrogens; s = secondary hydrogens; p = primary hydrogens.



tert-Butyl Chloride. For producing tertiary olefins from saturated hydrocarbons, tert-butyl chloride has been used as a chlorinating agent in a process involving chlorination followed by dehydrochlorination [159].

Tertiary olefins are olefins in which at least one of the double-bonded carbon atoms is single-bonded to each of two carbon atoms which can be constituents of either saturated acyclic or saturated alicyclic radicals. Examples are 2,3-dimethylbutenes and 1-methylcyclohexene. The corresponding starting hydrocarbons are 2,3-dimethylbutane and methylcyclohexane.

The chemistry involved can be represented by the following equations:



The chlorination by tert-butyl chloride is catalyzed by aluminum chloride (Eq. 22). Oxidized charcoal is the catalyst for the dehydrochlorination step (Eq. 23). The hydrogen chloride produced in Eq. (23) reacts with isobutylene (2-methylpropene) to produce the tert-butyl chloride chlorinating agent in Eq. (24).

The advantages claimed for this chlorinating agent are: (1) Greater selectivity than elemental chlorine, with yield per pass of the desired chloride about 61 to 70%, and (2) hydrogen chloride, which is the by-product in usual chlorination-dehydrochlorination operations, is utilized effectively.

Chlorination Processes

In this section an overview of industrially important chlorination processes will be presented. Key features in each will be discussed. The intent is not to provide detailed descriptions of processes for individual chlorocompounds. To do

otherwise would mean a duplication of coverage under individual compound names which can be found elsewhere in this Encyclopedia.

The reader will soon realize, if he has not already, that several competitive ways are often available for the production of a given chlorocompound. The selection of the best process for a particular situation will depend on many factors, such as capacity, raw material and energy availability, environmental impact, accessibility to know-how, and product quality requirements, in addition to capital investment and manufacturing costs. These factors will be mentioned where appropriate.

The safety hazards involved in the manufacture, handling, and use of chlorinated hydrocarbons are significant, and have been described elsewhere [41, 51, 84, 160]. The impact of some of these compounds, such as vinyl chloride and chlorofluorocarbons, on humans and the environment has raised much controversy and has not been fully quantified at this time [2528, 129]. These health and ecological considerations will have a profound effect on the supply and demand for chlorocompounds [63, 111].

The process descriptions which follow are grouped according to the type of starting compound.

Chlorination of Saturated Aliphatics

Substitutive Chlorination

Substitutive Chlorination of Methane. Chloromethanes. Of the saturated aliphatics, the chlorine derivatives of methanes are produced in greatest quantity. Methyl chloride, methylene chloride, chloroform, carbon tetrachloride, dichlorofluoromethane, and trichlorofluoromethane all have a United States production rate over 100 million kg/yr. The first four are generally produced in a combined process by successive substitution chlorination of methane as shown in the flow sheet (Fig. 2).

High purity (99%) methane is the feed material of choice, as impurities reduce the yield of chloromethanes [101]. However, impure feeds containing ethane, CO, CO₂, etc. have been used successfully [164]. For enhancing the production of carbon tetrachloride, partially chlorinated materials are recycled.

The ratio of chlorine to methane in the feed depends in part on the product mix sought. A ratio of 0.25 to 0.3: 1 or lower on a molar basis is used for maximizing methyl chloride formation. The ratio is increased up to 3.5: 1 for producing CCl₄ [80, 138]. The effect of increasing the chlorine-to-methane ratio is to shift the selectivity to the more highly chlorinated methanes and to increase methane conversion.

The chlorination is generally carried out in the vapor phase by thermal means. Liquid-phase chlorination using photochemical activation is sometimes employed in secondary reactors to promote complete conversion of methane to CCl₄ [101]. Wide ranges of reaction temperatures have been reported [136, 138]. Like the ratio of chlorine to

methane in feed, different reaction temperatures

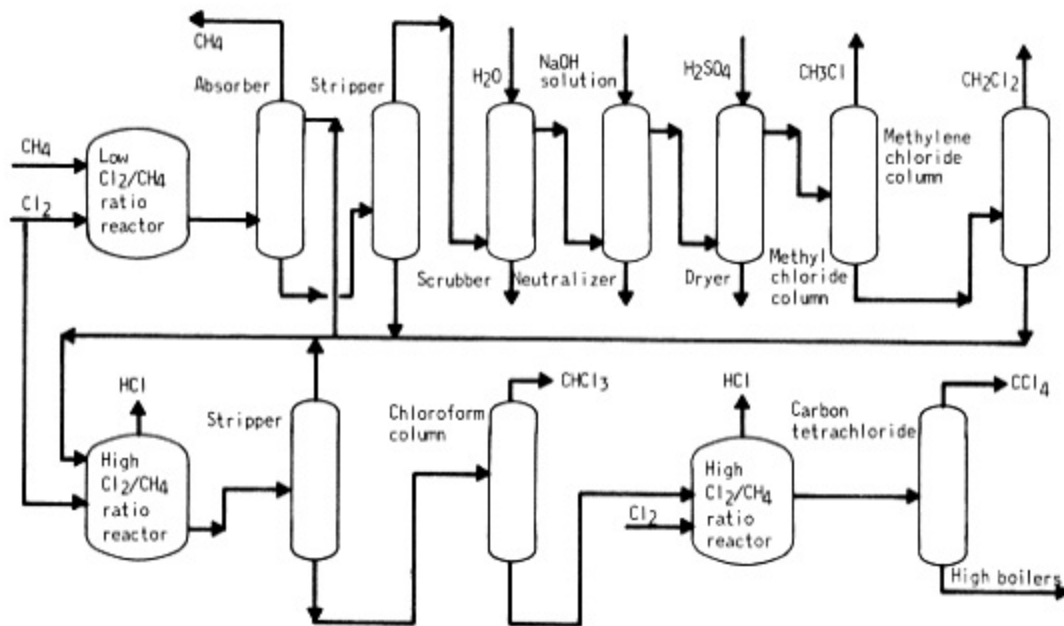


Fig. 2.

Flow sheet for substitutive chlorination of methane to produce methyl chloride, methylene chloride, chloroform, and carbon tetrachloride.

(From Austin [11] with permission of Chemical Engineering.)

may be selected depending on the desired product mix. Eisenlohr [49] recommended a temperature range of 370 to 425°C to enhance methyl chloride formation. A wider temperature range, 260 to 485°C, is acceptable for CCl_4 production.

Because the reaction is strongly exothermic, temperature control is a must from the standpoints of eliminating runaway reactions leading to explosion, chloromethane yield loss, and reactor corrosion. This is achieved by adjusting the chlorine-to-methane ratio in the feed. Optimum control of a reactor for thermal chlorination of methane has been analyzed [93]. For removing the heat of chlorination, numerous methods have been devised [64]. They include:

Using a large excess of hydrocarbon relative to chlorine in the feed.

Effecting chlorination in successive stages and distributing the chlorine feed.

Using diluent gases such as nitrogen, carbon dioxide, and recycled HCl .

Recycling chlorinated products.

Introducing the reacting gases into a liquid solvent and a molten salt bath [51].

Using precooled feed.

Using a "raining solids" technique in which precooled inert solids such as fused alumina sized 180 to 210 μm are dropped into the chlorination reactor countercurrent to the flow of gaseous reaction mixture. The solids are recycled continuously [39, 81].

The designs of chlorinators are proprietary. Two patented designs were developed by Viriot [158] and Eisenlohr [49]. Both designs make use of cooling jackets around reaction zones which are cylindrical chambers or tubes. The use of a massive fluid bed reactor for this application has been suggested and demonstrated in the laboratory [80]. The reaction kinetics and heat transfer for the chlorination of methane in a fluidized bed reactor have been analyzed [58, 59]. Nickel and steel as materials of construction for chlorinators are fairly satisfactory. Sometimes the reactor inner walls are lined with silica or ceramics [136].

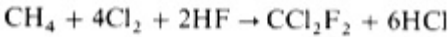
The effluent from the reactor is cooled and HCl is removed by water-washing. Subsequently, the reaction gas is scrubbed with caustic, dried by refrigeration or H_2SO_4 , and liquefied. The liquefied gas is fractionated by distillation. This pattern of product recovery is used between successive reactors as shown in the flow sheet (Fig. 2).

The reaction product consists of chloromethanes, HCl, and unreacted methane. Chlorine conversion is essentially quantitative. The conversion based on methane is 85 to 90%. Some carbon is also produced. The composition of chloromethanes can vary widely depending on feed composition and reaction conditions. In one commercial process using a chlorine-to-methane mole ratio of 0.6: 1.0 and a reaction temperature of 350 to 370°C, the chloromethanes are composed of 59% CH_3Cl , 30% CH_2Cl_2 , 9% CHCl_3 , and 2% CCl_4 [51]. For engineering design, a computational procedure for making the material balance around a chlorinator, or any chemical reactor, has been devised [95, 112].

From a safety standpoint, high velocities exceeding the rate of flame propagation should be maintained [51]. High reaction temperatures, or hot spots, should be avoided as the conversion of methane to carbon becomes significant above 570°C. The main requirements for successful chlorination of methane, as well as other hydrocarbons, are the use of correct feed composition, thorough mixing of chlorine and methane, and adequate means of temperature control which is necessary to avoid reaction runaways and explosions.

Chlorofluoromethanes. Dichlorodifluoromethane (Freon 12) and trichlorofluoromethane (Freon 11) can be produced by (1) fluorination of carbon tetrachloride with hydrogen fluoride and (2) chlorination of vinylidene fluoride which in turn is made by the addition of hydrogen fluoride to acetylene [51]. In 1969, Italy's Montecatini Edison S.p.A. began producing these chlorofluoromethanes by direct halogenation of methane, a less expensive raw material [69].

Referring to the flow sheet (Fig. 3), the feedstock consists of technical grade methane, anhydrous hydrogen fluoride, and liquid chlorine. When these are reacted over a catalyst in a fluidized bed reactor, substitutive chlorination of methane is believed to take place, followed by fluorination in which halogens are exchanged between the hydrogen fluoride and chlorine atoms contained in the chloromethanes. The overall reactions may be represented by



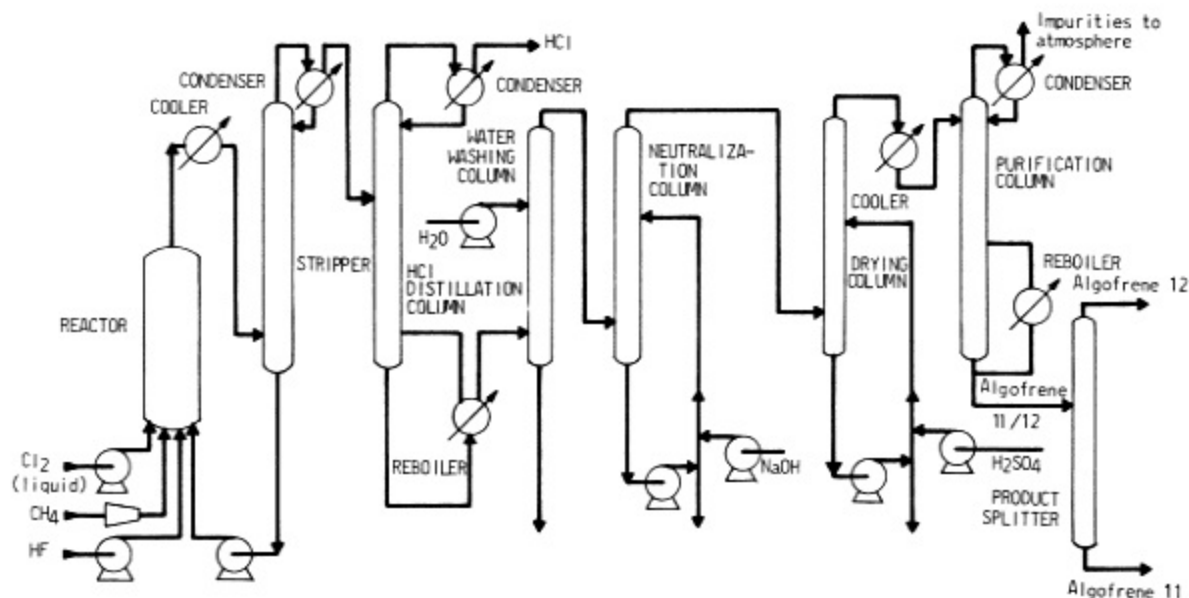


Fig. 3.

Flow sheet for halogenation of methane to produce dichlorodifluoromethane and trichlorofluoromethane.
(From Heath [69] with permission of Chemical Engineering.)

Reaction takes place at a temperature of 370 to 470°C and at a pressure of 400 to 600 kPa, with a contact time of 4 to 10s [76].

The gas leaving the reactor is sent to a distillation column where the reaction intermediates, containing a high concentration of CCl_4 (60 to 80% by weight), are bottom separated and recycled back to the reactor. Typically, 6 to 12 mol are recycled per mole of methane feed. This high recycle ratio provides a close temperature control of the reactor, promotes reaction selectivity, and apparently plays an important role in the process.

Further processing steps include (1) HCl by-product recovery by distillation; (2) washing and drying the chloromethanes mixture in a train of adsorption columns with water, caustic, and sulfuric acid; (3) condensation of the product; and (4) removal of low-boiling impurities by distillation. The product stream is further split by distillation, yielding 99.99% pure CCl_2F_2 and 99.96% pure CCl_3F .

The two chlorofluoromethanes are usually produced in equal amounts. The yields of CH_4 , Cl_2 , and HF claimed are 99, 97, and 94%, respectively.

In terms of raw material and energy usage, the requirements for producing 1000 kg of 50/50 mixture and 1480 kg of HCl by-product are as follows [76]:

CH_4	132 kg
Cl_2	2380 kg
HF	260 kg
Electric power	680 kWh
Steam at 1850 kPa	1700 kg
Steam at 500 kPa	1000 kg
Water	355 m ³

In addition to HCl, other by-products include carbon tetrachloride, trichlorofluoromethane, and perchloroethylene.

With minor modifications, this process can produce trichlorotrifluoroethane, dichlorotetrafluoroethane, and chloropentafluoroethane from ethylene [157].

Substitutive Chlorination of Ethane. Substitutive chlorination of ethane is much less common than that of methane and is also less studied. Generally, much of the technology for the vapor-phase chlorination of methane applies to ethane, propane, and higher homologs. The ease of chlorination increases with the number of carbon chains.

Light-catalyzed chlorination of ethane for ethyl chloride production has been commercialized but is uncommon [109]. That of ethane/methane mixtures at 100 to 200°C results in both ethyl chloride and methyl chloride [11]. Substitutive chlorination of ethane by thermal means is generally carried out at 250 to 500°C. The use of an inert fluid bed reactor to enhance temperature control has been reported [84]. Under high temperatures (600°C or higher) and short reaction times, vapor-phase chlorination of ethane can produce a variety of products [138]. These include ethyl chloride, vinyl chloride, vinylidene chloride, and trichloroethylene. Produced as by-products are perchloroethylene, cis- and trans-dichloroethylene, 1,1-dichloroethane, etc.

A combination of substitutive chlorination of ethane and hydrochlorination of ethylene for the manufacture of ethyl chloride has been reported by Shell Development Co. [73]. These two types of chlorination are carried out in two reactors in series, with the HCl produced in the substitutive chlorination step being utilized in the hydrochlorination step.

Into the first reactor are fed preheated ethane, gaseous chlorine, and a recycle gas stream containing unreacted ethylene. Chlorination is carried out adiabatically at or above 400°C. Ethyl chloride and hydrogen chloride are produced:



The conversion of chlorine in this reaction is complete. The reactor exit stream is cooled and sent to the first ethyl chloride column as shown in the flow sheet (Fig. 4). The bottoms from the column containing ethyl chloride and other chlorinated by-products are a part of the crude product. Hydrogen chloride, unreacted ethane, inerts, and some of the ethyl chloride are taken overhead. The overhead stream plus fresh ethylene are compressed, preheated, and fed to the hydrochlorination reactor. The mole ratio of ethylene to hydrogen chloride in this feed stream is kept at about 1:1.

The hydrochlorination reaction is carried out in the vapor phase at elevated pressure in the presence of a stationary catalyst:



Because of the importance of good temperature control for this reaction, a shell-and-tube type reactor is used. Thus the heat of reaction is removed and an isothermal condition is achieved by circulating heat exchange oil in the shell.

The hydrochlorinator exit stream is cooled and fed to the second ethyl chloride column where crude ethyl chloride is taken out as bottoms and the overhead consisting of ethane, inerts, unreacted ethylene, and hydrogen chloride is recycled to the chlorinator.

The combined crude ethyl chloride is purified in a straightforward manner by fractional distillation. Both light-ends and heavy-ends are removed.

The overall yield of this process is 90% for the hydrocarbons; that based on chlorine is 95%.

Substitutive Chlorination of Higher Paraffins. Straight-chain paraffins containing 10 to 30 carbons atoms have been chlorinated for a variety of end uses such as flameproofing and rot-preventive agents, plasticizer extenders, extreme-pressure lubricants, and as a source of olefin after dehydrochlorination. The technology involved in the substitutive chlorination of these higher paraffins has been covered adequately by Kirk and Othmer [84]. More recently, Hydrocarbon Processing [78] had a description of a commercial process offered by Wintershall AG Kassel.

Of recent interest because of their uses as intermediates in several petrochemical

processes is the production of monochlorides containing 11 to 14 carbon atoms [73]. The chlorination of paraffins in this molecular weight range

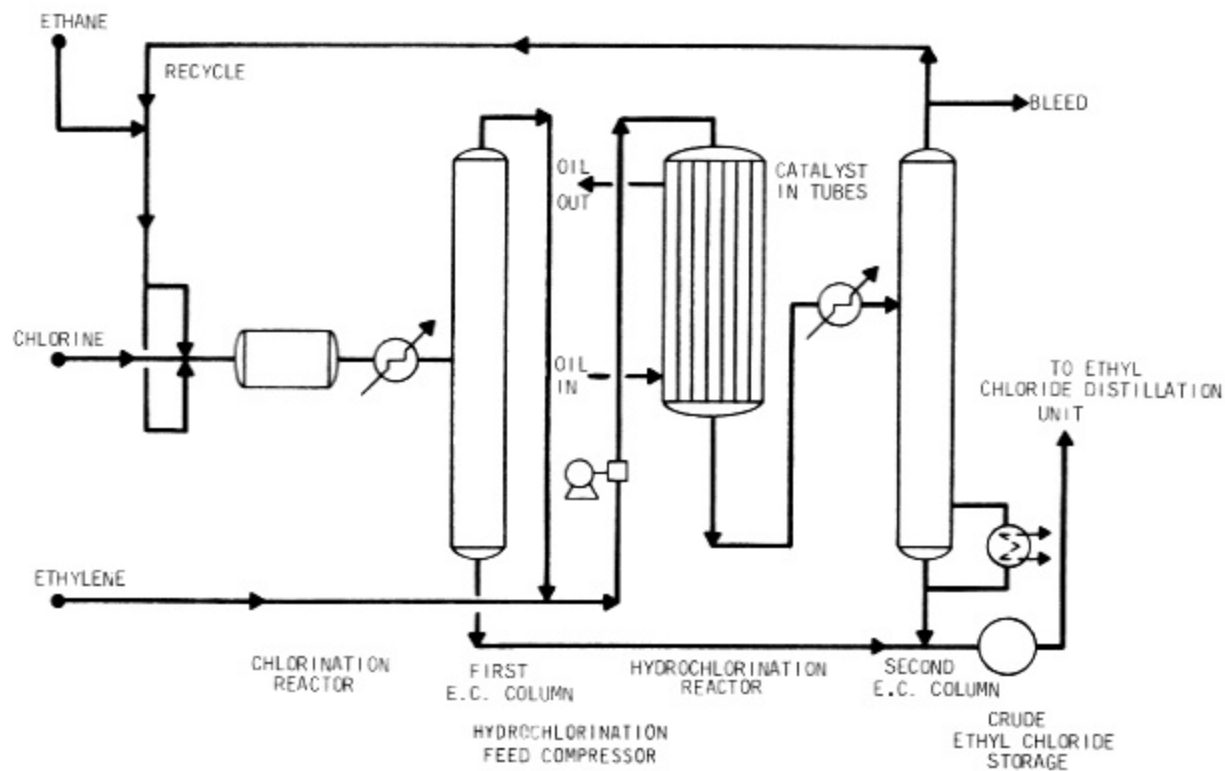


Fig. 4.

Flow sheet for substitutive chlorination of ethane and hydrochlorination of ethylene to produce ethyl chloride.
(From Hydrocarbon Processing [73] with permission.)

has been studied in the vapor phase [103] and in the liquid phase [71]. In vapor phase chlorination, high temperature (up to 500°C) and low conversion favor the formation of primary chlorides over secondary chlorides. Yields of primary chlorides as high as 50% have been reported.

For liquid-phase chlorination of normal paraffins, both stirred tank and plug flow reactors have been used. The stability and control of an adiabatic, continuously stirred tank chlorinator has been analyzed [46]. For the commercial development of their process, Phillips Petroleum selected a plug flow type chlorinator which was believed to enhance the yield of monochlorides [71]. At 30% conversion of paraffins, the selectivity to monochlorides was about 85%. Chlorine utilization was 100%. The operating conditions include: 310 to 790 kPa (absolute) pressure range, 32 to 71°C temperature range, and a mole ratio of paraffin to chlorine of 9:1. Care was taken to remove moisture and oxygen in the feeds. Photochemical rather than thermal or catalytic means of promoting the reaction was selected because of less reactor plugging and fouling.

The use of heuristic synthesis, optimization, and parametric sensitivity to identify and select processing arrangements for the manufacture of monochlorodecane has been proposed by Powers [117]. The hazards involved in chlorinating paraffins with this molecular weight range are depicted in an accident report [44].

Oxychlorination

Oxychlorination of Methane. In addition to substitutive chlorination, chloromethanes can also be produced by oxychlorination of methane. One such method is the Transcat Process developed jointly by The Lummus Co. and Armstrong Cork Co. [30, 122, 123].

The flow sheet for the Transcat Process (Fig. 5) consists of four primary sections, namely, a reactor section, an oxidizer effluent processing section, a chlorinator/oxychlorinator effluent processing section, and a distillation section for separating chloromethanes. The chemistry and several key features of the process have been described earlier under "Types of Chlorination."

The feed for the Transcat Process consists of methane and chlorine or HCl. In place of methane, an ethane feedstock can also be used [31]. Waste chlorocarbons recycled from the chloromethanes separation section and other chlorination processes can be utilized to augment the chlorine source.

The process makes use of three reactors. In the by-product pyrolysis reactor, chlorine values are recovered from the waste chlorocarbons mentioned above. Operated at approximately 1050°C and 600 kPa, the reactor converts the waste chlorocarbons, air and sometimes supplementary fuel to hydrogen chloride, chlorine, carbon dioxide, and water. These pyrolysis off-gases are fed to the middle of the oxidation reactor which is a brick-lined tower with two ceramic packed sections. Entering from the top is a stream of molten salt, consisting primarily of cuprous chloride, cupric chloride, and potassium

chloride. Flowing upward from the bottom of the reactor are air feed and pyrolysis gases. Reaction conditions are approximately 430°C and 600 kPa

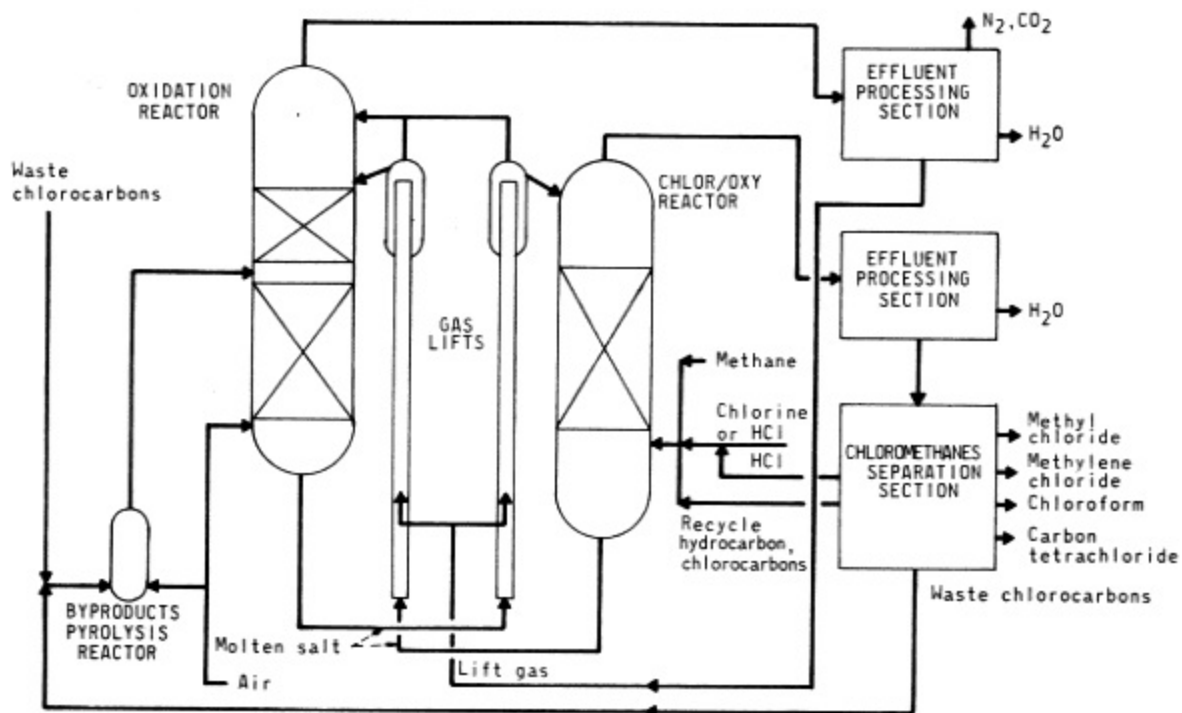


Fig. 5.
Flow sheet for oxychlorination methane to produce chloromethanes.
(From Chemical Engineering [31] with permission.)

(absolute). The molten salt leaving the oxidation reactor contains copper oxychloride, cupric chloride, and potassium chloride. The off-gases are sent to the oxidizer effluent processing section. From there a portion is recycled as lift gas which hydraulically lifts molten salt for both oxidation and oxychlorination reactors.

The design and the operating conditions of the oxychlorination reactor are similar to those for the oxidation reactor. The conversion of hydrocarbon feed to chlorohydrocarbon product is catalyzed by the molten salt. The salt releases the oxygen and chlorine picked up previously, then exits for circulation back to the oxidation reactor. The reaction product, consisting of unreacted methane, chloromethanes, carbon dioxide, water, and a small amount of C₂ chloro compounds, is passed on to the chlor/oxy effluent processing section where it is washed with dilute alkali to remove CO₂ and water. Distillation finally separates the stream into the desired products: HCl, intermediates, unconverted hydrocarbons for recycle, and by-product residues for burning.

The composition of the chloromethanes product is a function of conversion level and the degree of recycling unwanted chloromethanes. It can be tailored over wide ranges. Overall yield are 99 + mol% on chlorine and 75 to 90 mol% on methane.

Typical operating and cost data are shown in Table 3 [30].

Oxychlorination of Ethane. Oxychlorination of ethane to produce vinyl chloride monomer (VCM), trichloroethylene (TCE), perchloroethylene (PCE), and dichloroethane is claimed by C-E Lummus, the licensor of the Transcat Process [30]. The use of ethane as a raw material in place of the more expensive ethylene or acetylene has aroused considerable interest.

TABLE 3 Operating and Cost Data

	Chloromethanes ^a	Carbon Tetrachloride
Production rate, million kg/yr	113.5	90.8
Battery limits capital cost, ^b million \$	11.9	11.8
Methane, million kg	23.2	13.0
Chlorine, million kg	96.2	
Hydrogen chloride, million kg		86.6
Catalyst and chemicals, \$	150,000	250,000
Steam (4.1 MPa, 400°C), million kg	237	236
Condensate return (150°C), million kg	227	227
Cooling water ($\Delta T \approx 13^\circ\text{C}$), million liters	28,675	22,670
Electricity, million kWh	20.1	23.6
Fuel, million kcal	5,800	6,300
Operating labor, men/shift	4	4

^aFor 1/5 methyl chloride, 1/3 methylene chloride, 2/5 chloroform.

^bU.S. Gulf Coast, 4th quarter 1973 (initial fill of catalyst included).

TABLE 4 Specifications for Ethane and Chlorine Feeds

Ethane Specifications

Purity, vol. %	98.5
Methane, vol. %	1.0
Propane, vol. %	0.5
Sulfur, ppm max	2

Chlorine specifications

Purity, vol. %	98.0
Hydrogen, vol. %	0.4
Nitrogen, vol. %	0.8
Oxygen, vol. %	0.2
Carbon dioxide, vol. %	0.6
Water, ppm	50

Details of the Transcat Process have been presented earlier under "Types of Chlorination" and "Oxychlorination of Methane." The hardware used for methane is equally applicable here, and the process flow sheets for both are identical.

Although ethane is the cheapest by comparison, ethylene, ethyl chloride, or mixtures of these with ethane are also acceptable. The flexibility of the chlorine source has been described under "Oxychlorination of Methane." Typical specifications for ethane and chlorine feeds are given in Table 4 [122].

The overall yield of chlorine is 99 + mol%. That of ethane to VCM is about 80 mol%. When coproducing VCM, trichloroethylene, and perchloroethylene,

TABLE 5 Design Specifications for VCM

Specification	Value
Purity (dry basis), %VCM	99.9
Appearance	Clear and free of suspended matter
Water, ppm max	300
Acidity (as HCl), ppm max	1
Iron (as Fe), ppm max	0.5
Aldehydes (as acetaldehyde), ppm max	5
Sulfur (as S), ppm max	2.5
Acetylene, ppm max	2
Acetylenic compounds, ppm max	10
1,3-Butadiene, ppm max	2
Nonvolatile content, ppm max	500
Methyl chloride, ppm max	10
n-Butane, ppm max	50
Butene-1, ppm max	15
Butene-2, ppm max	1

TABLE 6 Operating and Cost Data for Producing VCM and VCM, TCE, and PCE Coproduct

	VCM	VCM, TCM, PCE
Production rate, million kg/yr	340.5	227/33.6/33.6
Battery limits capital costa	25	22.4
Ethane, million kg	205	137
Chlorine, million kg	195	187
Catalyst and chemicals, \$	220,000	200,000
Steam (4.1 MPa, 400°C), million kg	1,267	1,094
Condensate return (150°C), million kg	1,205	1,041
Cooling water ($\Delta T \approx 13^\circ\text{C}$), million liters	128,800	111,355
Electricity, million kWh	112	97
Fuel, million kcal	6,800	6,300
Operating labor, men/shift	5	5
aU.S. Gulf Coast, 4th Quarter 1973 (initial fill of catalyst included).		

the yield on ethane is about 90 mol%. A set of design specifications for VCM product is presented in Table 5 [122].

Typical operating and cost data for producing VCM and VCM, TCE, and PCE coproduct are shown in Table 6 [30].

Another set of economic estimates comparing the production costs of two grades of VCM and those for a conventional balanced ethylene process is given in Table 7 [122].

Chlorination of Unsaturated Aliphatics

Chlorination of Ethylene

Ethylene is the primary source of many chlorinated C₂ compounds. Vinyl chloride, ethyl chloride, ethylene dichloride, trichloroethylene, perchloroethylene, trichlorotrifluoroethane, dichlorotetrafluoroethane, chloropentafluoroethane, etc. are commercially important and can all be derived from ethylene. Several manufacturing processes for these chemicals using a mixture of ethylene and ethane as feed have been mentioned under "Chlorination of Saturated Aliphatics."

In chlorinating ethylene, several types of chlorination often take place in a single reactor or an integrated process. Therefore, in the ensuing discussion of exemplary processes, some overlap in the coverage of different types of chlorination is unavoidable.

Substitutive Chlorination of Ethylene. Substitutive chlorination of ethylene offers the potential of producing vinyl chloride directly, thus avoiding the manufacture of ethylene dichloride as an intermediate. Although a number of patents have been issued, commercial processes based on this route are not well

TABLE 7 Transcat Capital and Manufacturing Costs

	Transcat VCM at 99.9% Purity	Transcat VCM at 99.6% Purity	Balance Ethylene Oxychlorination with Waste Incineration
Capital cost, millions \$			
Battery limits capital cost	15.7b	14.6b	13.6c
Chlorinated waste incineration			1.9d
Total	15.7	14.6	15.5
Raw materials			
Ethane at 2.64¢/kg	1.59	1.59	
Ethylene at 8.15¢/kg			3.88
Chlorine at 5.07¢/kg	2.91	2.91	3.02
Catalyst and chemicals	0.04	0.04	0.11
Total	4.54	4.54	7.01
Utilities	0.84	0.84	0.62
Operating labor	0.11	0.11	0.11
Maintenance	0.31	0.29	0.31
Overhead expenses			
Labor overhead	0.13	0.13	0.13
Local insurance and taxes	0.11	0.09	0.11
Depreciation	0.68	0.64	0.68
Total	0.92	0.86	0.92
Total cost of production, ¢/kg	6.72	6.64	8.97

aProduct contains about 4000 ppm butane/butene impurities.

bIncludes catalyst inventory and by-products pyrolysis reactor.

cThe battery limits construction cost of \$13.4 million is from Spitz [141] with escalation to 1973.

dThe battery limits construction cost for chlorocarbon incineration with HCl recovery is 1.9 million \$ for 11.4 million kg/year feed based on Ref. 33.

developed. One such process, which also produces trichloroethylene, dichloroethane, and trichloroethane along with vinyl chloride, was commercialized by Produits Chimiques Perchinery-Saint-Gobain, Neuilly, France [76]. This so-called Chloe Process consists of three basic parts [125].

Hot Chlorination. Using ethylene and chlorine, along with recycled di- and trichloroethane, substitutive chlorination, additive chlorination, and dehydrochlorination all take place in the vapor phase, yielding vinyl chloride monomer, dichloroethylene, tar, and heavy chlorinated solvents. The reactor is a stainless steel vessel, simple in design and containing no catalyst. The operating temperature and pressure are 370 to 500°C and 150 kPa, respectively. Effluent from the reactor is piped to a series of five distillation columns for product separation and purification as shown in Fig. 6.

Cold Chlorination. Here additive chlorination of dichloroethylene from the Hot Chlorination Section produces tetrachloroethane at 52°C, atmospheric pressure, and in the absence of a catalyst. Tetrachloroethane is dehydrochlorinated to trichloroethylene by thermal cracking.

Oxychlorination. Referring to the flow sheet, hydrochloric acid from the Cold Chlorination Section and hydrochloric acid/ethylene from the Hot Chlori-

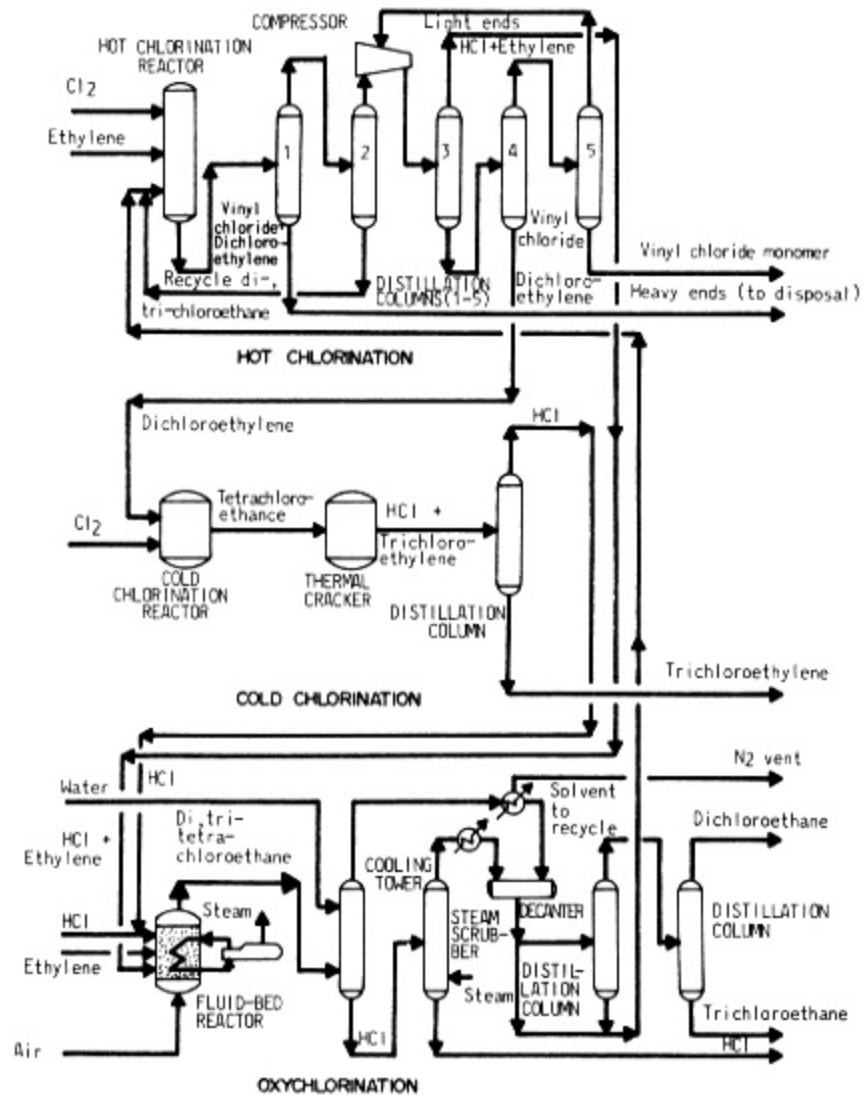


Fig. 6.
Flow sheet for direct chlorination of ethylene to produce trichloroethylene,
dichloroethane, and trichloroethane.
(From Rosenzweig [125] with permission of Chemical Engineering.)

nation Section are fed to a fluid-bed oxychlorinator. So are some additional feed hydrochloric acid and ethylene. The reactor, containing a catalyst (an active copper salt over an oxide substrate), is operated at 200 to 800 kPa and 280 to 480°C. Di-, tri-, and tetrachloroethane and water are formed. HCl recovery and product purification are achieved by condensation, steam scrubbing, and fractional distillation in succession.

A 94.5% yield of useful products for the overall process, measured in terms of carbon, is reported.

High flexibility for the product mix is claimed. The ratio of vinyl chloride monomer to chlorinated solvents can range from 2.5:1 to 0.8:1; that of trichloroethane to dichloroethane can be from 0:1 to 0.2:1 in the oxychlorination step.

For an annual production of 120 million kg of vinyl chloride, 85 million kg of trichloroethylene, and 50 million kg dichloroethane, the cost of an operating plant located in France was \$15.5 million in 1970 dollars.

Additive Chlorination of Ethylene. Additive chlorination of ethylene produces ethylene dichloride, a precursor for vinyl chloride and other chlorinated compounds. Although the reaction can proceed either in the vapor or liquid phase, the latter is used in almost all commercial plants for more efficient utilization of the heat of chlorination, easier temperature control, and increased safety.

In a typical process, ethylene, chlorine, and a small amount of air are sparged into a pool of ethylene dichloride which contains a catalyst such as ferric chloride and which is maintained at a temperature ranging from 40 to 70°C. The temperature in the tower reactor is controlled either by the use of internal or external heat exchangers or by vaporization of ethylene dichloride [4]. From the reactor the effluent is chilled and the noncondensables are separated. This is followed by washing to remove impurities. The yield from ethylene is about 96 to 98% of theoretical.

Corrosion is always a problem for this type of process. Hence the feed streams must be dried to less than 30 ppm [132]. Although carbon steel is adequate as a material of construction for the reactor [37], nickel-based nonferrous alloys are often preferred.

An example of this process is one used and licensed by Diamond Alkali [73]. Several other processes have been described by Albright [4].

For the manufacture of vinyl chloride, additive chlorination of ethylene is often carried out in conjunction with oxychlorination of ethylene and dehydrochlorination of the combined ethylene dichloride. These three reaction steps are integrated, resulting in so-called balanced ethylene chlorination and oxychlorination processes. Several versions of this "balanced" process have been developed and commercialized. For convenience, the description of this type of process is covered under "Oxychlorination of Ethylene."

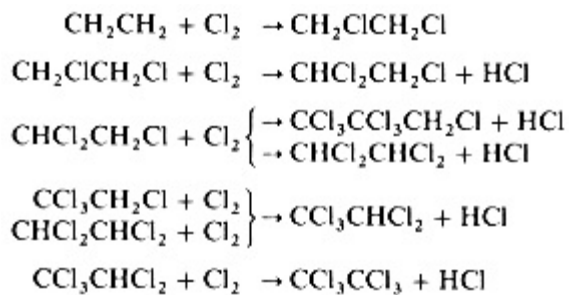
Another commercial process which makes use of additive chlorination of ethylene in part

produces trichloroethylene and perchloroethylene as co-products [82, 149]. Developed by Toagosei Chemical Co., Japan, the process

consists of two reaction steps: (1) additive and substitutive chlorination of ethylene, and (2) dehydrochlorination of chloroethanes.

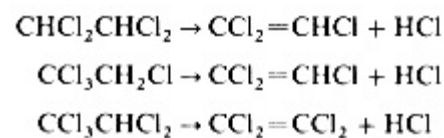
The feed chlorine must be free of oxygen as it inhibits the chain reaction in the direct chlorination step.

As shown in the flow sheet (Fig. 7), chlorine is fed to a packed-tower absorber where it is dissolved in a mixture of chloroethanes. This is then fed separately but cocurrently with ethylene into the bottom of a bubbling-tower reactor. The operating conditions in the reactor are 810 kPa and 100 to 130°C. Instead of a catalyst, Toagosei employs ethylene itself to accelerate the chlorination reaction. The reactions which occur in the reactor are summarized below:



For this reaction step the chlorine conversion is 100% and ethylene conversion ranges from 95 to 98%.

The reactor effluent is sent to a flash drum to remove unreacted ethylene and by-product hydrogen chloride. The rest is sent to a distillation column where di- and trichloroethane are taken overhead and returned to the reactor. Tetrachloroethanes, pentachloroethane, and trace hexachloroethane are transported to the cracking furnace where the following dehydrochlorination reactions take place:



The furnace is of the monotubular type and is operated at 910 kPa and 430 to 450°C. A small quantity of FeCl₃ is added to accelerate cracking and reduce carbon formation.

The conversions of tetra- and pentachloroethanes are 95 and 80%, respectively. After refining, the purity of both trichloroethylene and perchloroethylene exceeds 99.8 wt.%. The stabilities of these products are enhanced by adding a small amount of aliphatic amines, phenols, and/or epoxides.

For a plant producing 31 million kg of trichloroethylene and 4.8 million kg of perchloroethylene annually, the battery limit investment is \$2.8 million, based on Japanese construction costs in 1968. The corresponding raw materials and utilities requirements are shown in Table 8 [82].

TABLE 8 Raw Materials and Utilities Requirements for Producing Trichloroethylene and Perchloroethylene

Per 1000 kg products

Trichloroethylene	862 kg
Perchloroethylene	138 kg
Raw materials	
Ethylene	220 kg
Chlorine	1720 kg
By-product	
HCl (100%)	830 kg
Utilities	
Steam (340 kPa)	2400 kg
Steam (130 kPa)	2100 kg
Cooling water (32°C)	300 m ³
Process water (20°C)	25 m ³
Fuel oil	35 kg
Refrigeration (-30°C)	43 × 10 ³ kcal
Electricity	200 kWh
Nitrogen	65 m ³ at standard conditions

Hydrochlorination of Ethylene. The making of ethyl chloride by the hydrochlorination of ethylene accounts for about 88% of the total United States production [11]. The reaction proceeds at a temperature of 35 to 40°C and is promoted by acidic catalysts such as AlCl₃. Yield is around 90%. Adding ethylene dichloride to the reaction mixture reduces the yield of polychloro compounds. A Shell Development process combining substitutive chlorination of ethane and hydrochlorination of ethylene for the manufacture of ethyl chloride has been described earlier (see "Substitutive Chlorination of Ethane").

Oxychlorination of Ethylene. Numerous papers, patents, and processes on oxychlorination of ethylene have appeared in the last decade [4, 5, 18, 29, 43, 47, 7478, 102, 125, 141, 142]. The Lummus' Transcat Process described earlier under "Oxychlorination of Ethane" should be applicable to an ethane/ethylene feedstock as well. Two other processes will be delineated here for illustrative purposes.

In Vulcan's process, 1,2-dichloroethane is produced by oxychlorination of ethylene [43]. Nearly stoichiometric proportions of ethylene, anhydrous hydrogen chloride, and air are first mixed and used as feed. The high exothermic heat of reaction over 55 kcal/g-mol of product is removed by using a fixed-bed multiple-tube vertical reactor resembling a heat exchanger. The catalyst, which is supported on activated alumina and includes a copper salt, is fixed in the tubes, and coolant flows through the shell. Heat generated by the reaction is recovered as 70 kPa steam.

To moderate the temperature in the reactor, the catalyst is mixed with an inert diluent, such as graphite, and charged into each reactor tube in multiple zones of increasing catalyst concentration from inlet to outlet. Thus the average

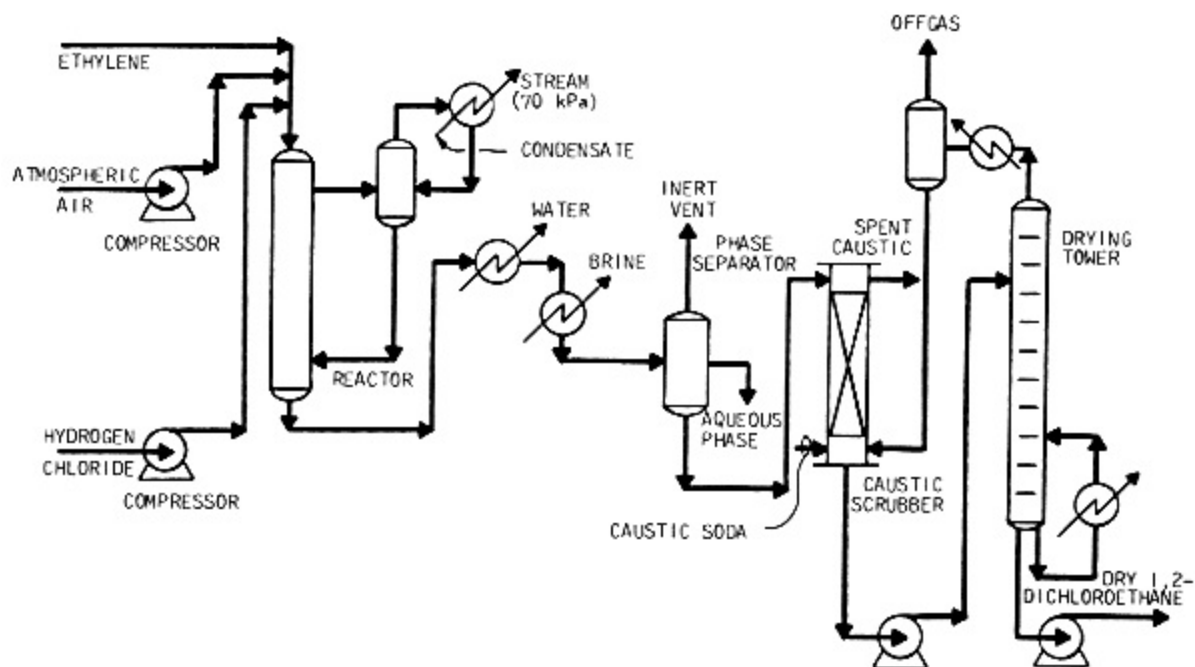


Fig. 8.
Flow sheet for oxychlorination of ethylene to produce 1,2-dichloroethane.
(From DeForest and Penner [43] with permission of Chemical Engineering.)

reaction temperature does not exceed 270°C, and high throughput per unit size is claimed.

Referring to Fig. 8, the effluent from the reactor is condensed in water-cooled and brine-cooled condensers, and the resultant condensate is collected in a phase separator operated at about 40 kPa pressure. Noncondensable gases, mostly nitrogen, are vented, and the aqueous stream is discharged to waste.

From the phase separator, the organic crude is passed on to a caustic scrubber where residual acidity and chloral (CCl₃CHO) are removed. The product is then dried by azeotropic distillation.

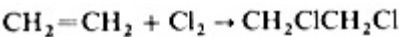
Depending on the composition of the feed, the conversions range from 92.8 to 96.8% for HCl and 93.5 to 94.0% for ethylene. Less than 2% of feed ethylene is converted to carbon oxides. A typical analysis of the dried product is given in Table 9 [43].

Utilities consumption per kg of crude 1,2-dichloroethane (no HCl compression and no purification of the product) is

Electricity (mainly air compression)	0.99 kWh
Steam (net production, 70 kPa saturated)	0.90 kg
Cooling water (32 to 38°C)	31.6 liters

As mentioned under "Additive Chlorination of Ethylene," the so-called balanced ethylene chlorination and oxychlorination processes make use of additive chlorination of ethylene and oxychlorination of ethylene, followed by dehydrochlorination of the combined ethylene dichloride (EDC). Thus vinyl chloride monomer is produced and hydrogen chloride by-product is utilized. One such process has been developed by Mitsui Toatsu Chemicals, Inc. [76].

In the direct chlorination area, ethylene and chlorine are sparged into a pool of EDC maintained at its boiling point.



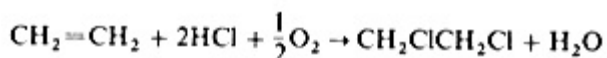
The heat of reaction is removed by vaporizing EDC.

TABLE 9 Analysis of Dried Product

	Wt. %
trans-1,2-Dichloroethylene	0.01
1,1-Dichloroethane	0.01
cis-1,2-Dichloroethylene	0.03
Chloroform	0.35
Carbon tetrachloride	Trace

1,2-Dichloroethane	98.5
Trichloroethylene	Trace
1-Bromo-2-chloroethane	0.02
1,1,2-Trichloroethane	1.0
1,1,2,2-Tetrachloroethane	0.10

Oxychlorination is carried out in a fluidized bed reactor under moderate pressure. The feed consists of oxygen, ethylene, hydrogen chloride, and recycle gas from the Caustic Scrubber (see flow sheet in Fig. 9). For safety reasons, care is taken to keep the composition of the feed mixture within the nonflammable region.



The heat of reaction is removed by circulating water under pressure and recovering it as steam. Good temperature control in the fluidized bed reactor is essential to maintain high selectivity and is the subject of an independent study [90]. From the fluidized bed reactor, the effluent is cooled, and both the EDC and water produced are condensed in a quencher. Noncondensed gases are recycled back to the reactor. EDC is washed by caustic, separated from water by decantation, and is further dehydrated.

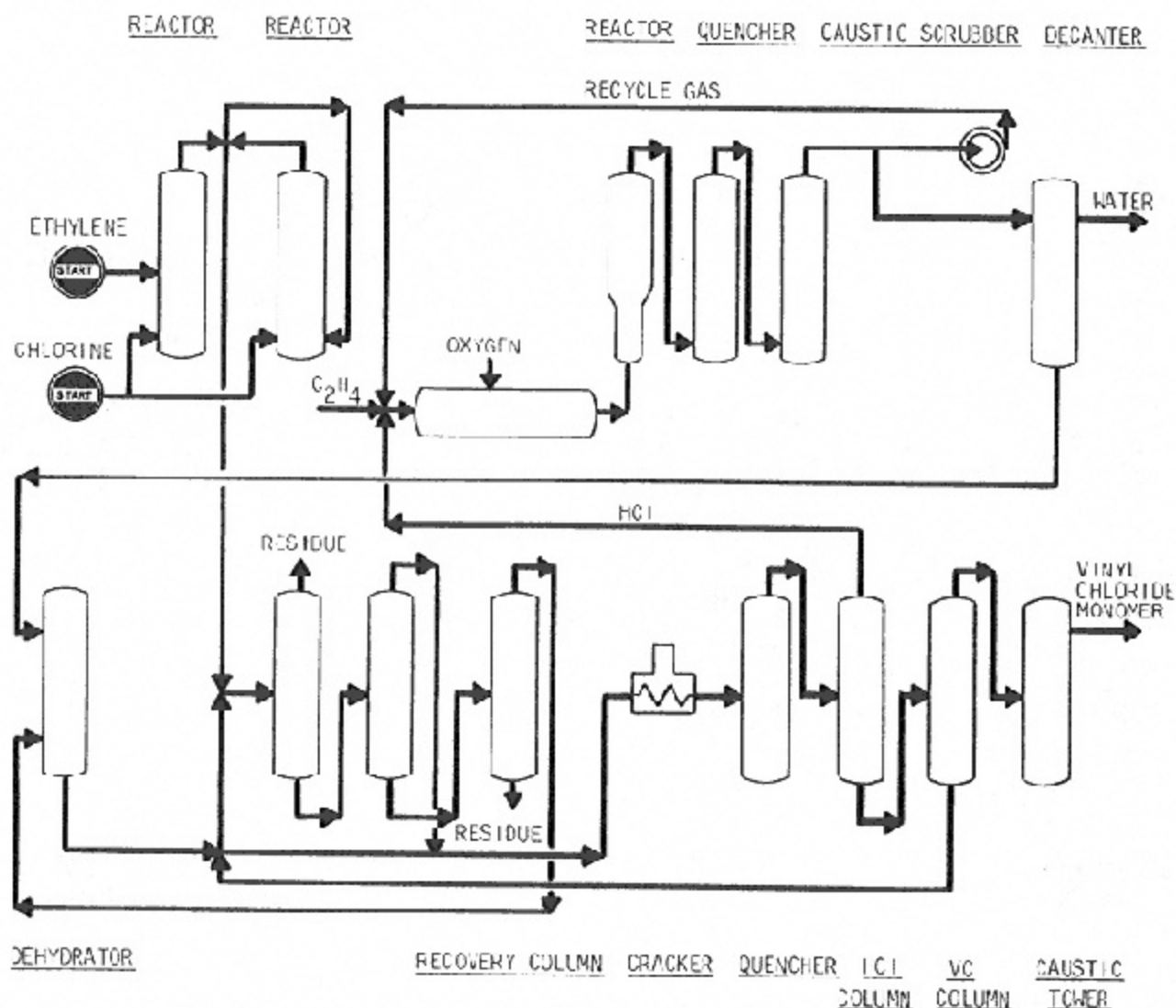


Fig. 9.

Flow sheet for additive chlorination and oxychlorination of ethylene, and dehydrochlorination of ethylene dichloride to produce vinyl chloride.

(From Hydrocarbon Processing [76] with permission.)

TABLE 10 Raw Materials and Utilities Requirements per Ton of VCM

Raw materials	
Eehylene (as 100%)	0.470 ton
Chlorine (as 100%)	0.607 ton
Oxygen (as 100%)	0.138 ton
Fuel	1.15 × 106 kcal
Utilities	
Electric power	130 kWh
Steam	0.96 ton
Process water (deionized)	0.45 ton

Prior to dehydrochlorination, often called cracking or pyrolysis, the combined EDC from direct chlorination and oxychlorination is purified by fractional distillation. The purified EDC is cracked to vinyl chloride monomer (VCM) and hydrogen chloride under high temperature and high pressure conditions:



From the cracker, the hot effluents are quenched and then sent to the VCM purification area. (See "Dehydrochlorination of Alkyl Chlorides" below for additional information.)

Purification of VCM is accomplished by removing HCl and EDC in two distillation columns. Hydrogen chloride is returned to the oxychlorination area. VCM is further dried in a caustic column before emerging as a finished product.

The raw materials usage and utilities requirements per ton of VCM are presented in Table 10 [76].

VCM product has the specifications presented in Table 11 [76].

Chlorination of Acetylene

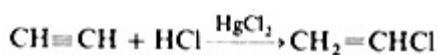
Up until a few years ago, acetylene was the primary source for vinyl chloride and a number of other chlorinated C2 compounds. However, because of the

TABLE 11 VCM Product Specifications

Vinyl chloride	min 99.99% by weight
Hydrogen chloride	max 0.1 ppm
Iron	max 0.1 ppm
Acetylenic compounds	5 ppm
Chloro compounds	max 50 ppm
Water	max 70 ppm
Butadiene	max 6 ppm

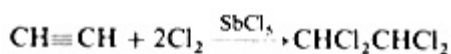
prevailing price structure, acetylene has been largely replaced by ethylene and ethane as raw materials.

Hydrochlorination of acetylene at 90 to 140°C in the presence of a mercuric chloride-based catalyst leads to vinyl chloride [11]:



Typically, the yield of vinyl chloride ranges from 80 to 85%. The raw material consumption is 440 kg acetylene, 600 kg anhydrous hydrogen chloride, and 1 kg mercuric chloride per 1000 kg vinyl chloride [51].

Additive chlorination of acetylene in the presence of antimony pentachloride produces tetrachloroethane [108]:



A powerful but toxic solvent, tetrachloroethane is also a starting material for making trichloroethylene and perchloroethylene [11].

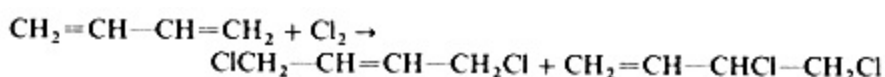
Since these processes find limited applications nowadays, the reader is referred to existing literature for details [84, 108].

Chlorination of Butadiene

Additive chlorination of butadiene can lead to the formation of chloroprene (2-chlorobutadiene-1,3). In a continuous process developed by the Distillers Co. Ltd. in the mid-1950s and later acquired and commercialized by BP Chemicals Ltd., London, vapor-phase chlorination of butadiene is followed by isomerization of the dichlorobutenes which can be dehydrochlorinated to chloroprene for the manufacture of polychloroprene rubbers [14]. This process should compete favorably against the classical dimerization/hydrochlorination process using acetylene. Details follow.

The chlorine and butadiene feed must be dry and essentially oxygen-free. This specification is necessary in order to minimize side reactions leading to light and heavy boilers formation in the initial chlorination stage. The use of butane, 1-and 2-butenes, or mixtures of these with butadiene as a feedstock is feasible if the production of by-product hydrogen chloride is acceptable. Isobutane and isobutene should be absent in the feed to avoid complications in the purification stage.

Referring to the flow sheet (Fig. 10), vapor-phase chlorination of butadiene is carried out at about 300°C, resulting in a mixture of cis- and trans-1,4-dichlorobutenes-2 and 3,4-dichlorobutene-1 [14]:



To maximize 3,4-dichlorobutene-1, which is the desired product, the relative

concentrations of the isomers in this mixture can be altered by heating

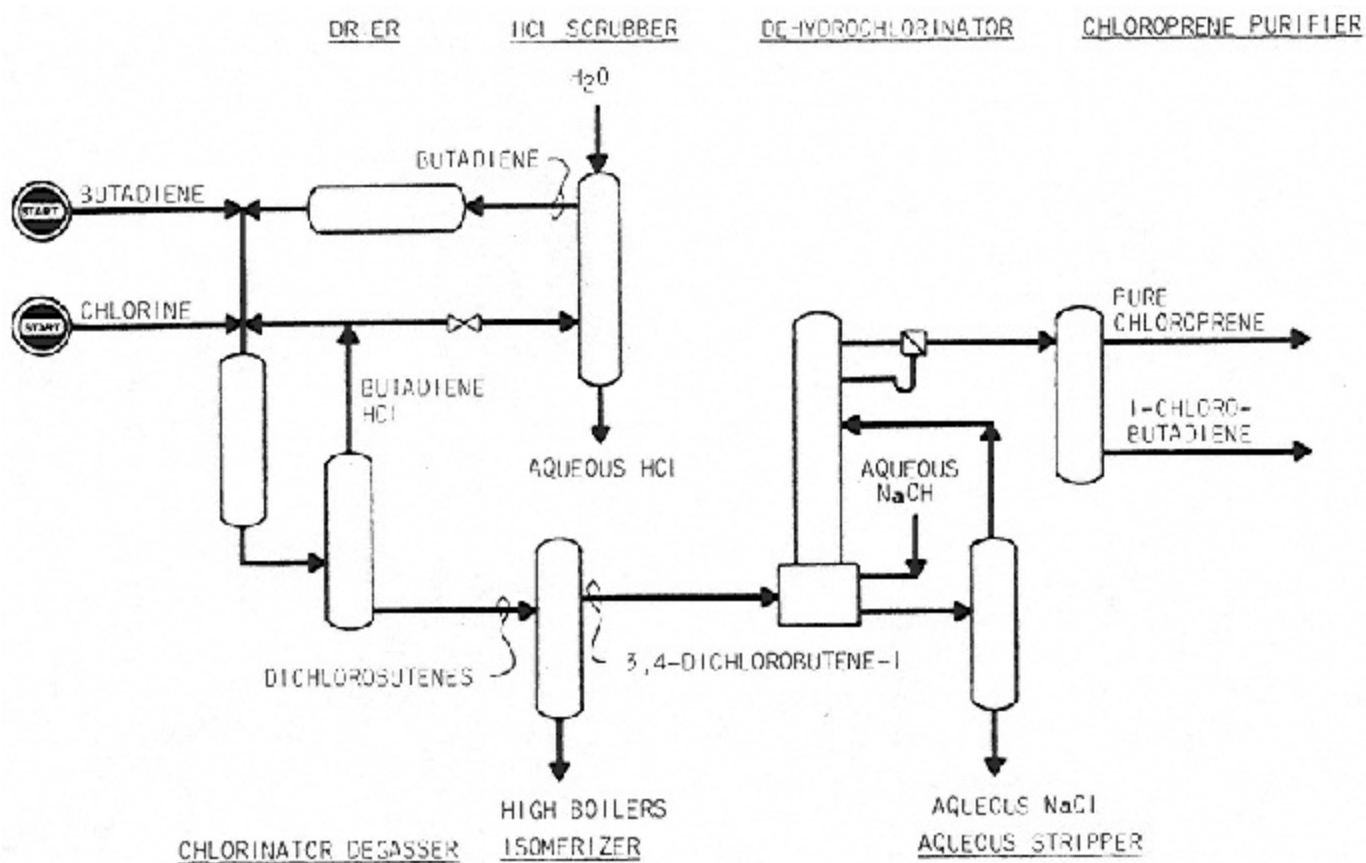
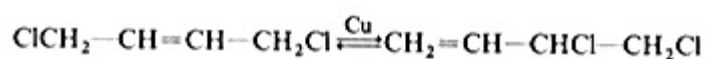


Fig. 10.

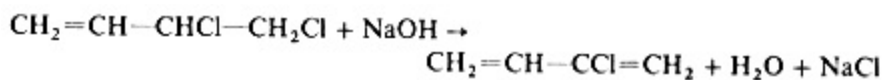
Flow sheet for chlorination of butadiene to produce chloroprene.
 (From Bellinger and Hollis [14] with permission of Hydrocarbon Processing.)

in the presence of copper and other metallic salts:



3,4-Dichlorobutene-1 can be separated readily from the other isomers by distillation.

Dehydrochlorination of 3,4-dichlorobutene-1 follows the isomerization stage and is effected by heating with aqueous alkali which removes one chlorine atom as alkali chloride:



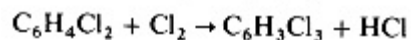
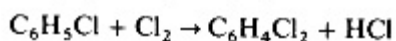
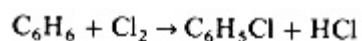
The resultant chloroprene is purified by fractionation from which traces of 1-chlorobutadiene-1,3 are removed and unreacted dichlorobutene is recycled. Typically the product has an assay of 98.5% by weight, the primary impurity being 1-chlorobutadiene present in 1%.

Chlorination of Aromatics

Chlorination of Benzene

Chlorination of benzene leads to chlorobenzene, o- and p-dichlorobenzene, hexachlorobenzene, hexachlorocyclohexane, and others. These compounds, in turn, are used to manufacture phenol, aniline, DDT, chloronitrobenzenes, etc. and find end uses such as dye intermediates, insecticides, solvents, heat transfer fluids, degreasing agents, deodorants, and azeotrope-forming agents.

Substitutive Chlorination of Benzene. Chlorine can be substituted into the benzene ring under mild conditions (40 to 70°C and atmospheric pressure) in the presence of a catalyst to give three products: monochlorobenzene (MCB) and o- and p-dichlorobenzene (DCB). The formation of m-dichlorobenzene and polychlorobenzenes also occurs but to a much lesser extent. The reactions can be represented by the following overall equations:



and so on. These substitutive chlorination reactions are thought to proceed by means of an ionic mechanism. Typically, the yield is 70 to 75% for chlorobenzene and 20 to 10% for dichlorobenzenes. The ratio of p-DCB to o-DCB is 2 to 3:1 [51].

The most common catalyst for this chlorination is ferric chloride, although fuller's earth and chlorides of aluminum, tin, and other metals are also used.

Sometimes this ferric chloride catalyst is prepared in situ by adding iron turnings to the reactor [66]. The relative merits of various metal chlorides as catalysts and their chemistry have been studied by Kovacic [91] and Olah [113].

For commercial processes, both benzene and chlorine feeds should be dry (say, about 20 to 35 ppm maximum water content), as water deactivates the catalyst, causes corrosion, and increases high-boiler formation. Also detrimental to yield is the presence of high boiling hydrocarbons and nonaromatics in the benzene feed [66].

Chlorination is effected by contacting gaseous chlorine with liquid benzene in a tall cast-iron or steel vessel lined with lead or glass and fitted with a reflux condenser and cooling coils. In a batch process, temperature control of the reactor is regulated by the chlorine addition rate, and the progress of the reaction can be checked by density measurements. In a continuous process a combination Chlorination and fractionization apparatus may be used to minimize the formation of higher chlorinated products. Thus MCB is isolated as it is formed, and unreacted benzene is constantly exposed to chlorine [51]. When the process is operated efficiently, a yield of chlorobenzene as high as 95% has been reported [84].

A step-by-step procedure for designing a continuous stirred tank reactor for chlorinating benzene has been depicted by Barona [13]. The use of analog computers to simulate and control benzene chlorination has been investigated [19, 94]. Clearly, backmixing in a continuous reactor hinders MCB yield.

Several means for increasing the MCB to DCB ratio in the product include:

Use a low reaction temperature, e.g., 30 to 40°C

Use a low chlorine-to-benzene mole ratio in the feed, e.g., 0.6:1.

Keep conversion per pass low

On the other hand, p-DCB can be produced in high yield as a primary product by using aluminum chloride as catalyst.

Hydrogen chloride evolved during the reaction is recovered as hydrochloric acid by scrubbing. Water, o-dichlorobenzene, and sometimes oil have been used as scrubbing media [51].

The liquid effluent from the reactor is washed with water and caustic soda in succession. The decanted organics are separated and purified by fractional distillation and crystallization. Benzene is recovered by distillation and recycled. Chlorobenzene is recovered in another column. The dichlorobenzenes and other chlorinated compounds are resolved by first crystallizing out p-DCB which is later purified by vacuum distillation. The mother liquor from the crystallizer is sent to a distillation column in which o-DCB is recovered as a bottom product. Some recycling in this separation area is necessary in

order to achieve the desired product purities.

Oxychlorination of Benzene. Like the aliphatics, oxychlorination of benzene has gained considerable interest in recent years as a means of utilizing relatively inexpensive hydrogen chloride. This interest is reflected by the large number of pertinent patents issued in the United States and abroad.

The early development of the Raschig process for converting benzene to chlorobenzene (and ultimately to phenol) was reviewed briefly under "Types of Chlorination." Gulf's liquid-phase oxychlorination process catalyzed by nitric acid was also described earlier [130].

Another published process which makes use of oxychlorination technology is the Hooker phenol process [75, 118] which is an outgrowth of the original Raschig version. Like its predecessor, the Hooker process consists of two distinct steps: the oxychlorination step for converting benzene to monochlorobenzene (MCB) is followed by the hydrolysis step for converting MCB to phenol. For the purpose of illustrating the technical aspects involved in the oxychlorination, only the first part of the process is discussed below.

Hydrochloric acid feed is vaporized and mixed with air. This mixture in turn is combined with benzene vapors at 300°C prior to entering the oxychlorinator. In the reactor, about 90% of the benzene reacting goes to MCB. The rest is converted to dichlorobenzenes and small amounts of more highly chlorinated benzenes. The conversion is probably low of the order of 10%. The effluent from the oxychlorinator is fed into a column which separates the chlorinated benzene and water at the bottom from benzene and nitrogen at the top. A centrifugal blower located at the end of the system creates a slight vacuum in the reactor and the column. This vacuum moves the reactants through the equipment and prevents leakage to the outside.

Based on Hooker literature [118], the popular notion about the corrosive nature of the process is imaginary. The process streams containing hydrochloric acid with or without water can be handled by steel above 130°C. Below that temperature, acid-proof materials of construction such as stoneware, porcelain, or Karbate are satisfactory.

To handle the exothermic heat of oxychlorination, Hooker divides the catalyst into a number of beds in series and injects subcooled reactants between them. This arrangement reportedly is preferred over the use of interior cooling surfaces.

The advantages of this process include little auxiliary chemical consumption and little effluent for disposal. For manufacturing phenol, however, a number of competitive processes should also be considered.

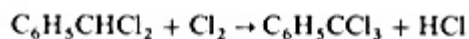
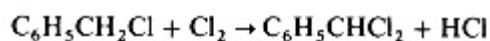
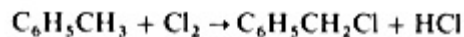
Chlorination of Toluene

Chlorine can substitute a hydrogen in toluene in the ring to form chlorotoluene or on the methyl group to form benzyl chloride. The latter, produced in large quantity, is industrially more important. Benzyl chloride is used chiefly in the manufacture of butyl benzyl phthalate and benzyl alcohol. It is also a raw material for numerous derivatives such as flavor and perfume chemicals, pharmaceuticals, disinfectants, and dyes.

The use of low temperature (30 to 50°C) and a catalyst such as iron in the chlorination of toluene favors the formation of chlorotoluene. On the other hand, chlorinating boiling

toluene at 120 to 130°C in the dark produces benzyl chloride. In the presence of radiation (light, beta radiation, etc.), further chlorination is promoted, resulting in benzal chloride and benzotrichloride.

Sometimes a chlorine-carrier such as PCl_5 and FeCl_3 is used as a catalyst to enhance complete chlorination.



The kinetics of these three consecutive, irreversible reactions have been studied [165]. The rates are found to be first order with respect to the organic substrate. As such, and to maximize benzyl chloride formation, batch or plugflow continuous reactors are preferred. The factors involved in the design of bubble column reactors for chlorinating toluene have been studied by Fong [53]. Iron impurities hinder the reaction. Therefore, glass- or lead-lined equipment is generally chosen for this application.

Typically, the yield of benzyl chloride is about 90%. Those of benzal chloride and benzotrichloride are 9 and 1%, respectively. Chlorotoluene is also formed in trace quantities. Some control over the product mix can be achieved by regulating the ratio of chlorine to toluene in the feed. A low chlorine/toluene ratio favors benzyl chloride formation. As in benzene chlorination processes, the density of the reaction mass can be used to monitor conversion.

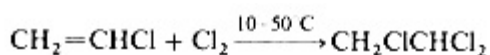
The reaction crude is washed with mild alkali. Subsequently, the individual chlorocompound is separated and purified by distillation. Commercial benzyl chloride is usually stabilized and stored in stainless steel drums [156].

Chlorination of Other Compounds

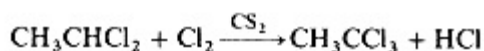
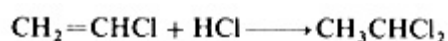
Chlorination of Aliphatic Chlorides

Under this heading can be included several industrially important chlorination reactions which have not been discussed above.

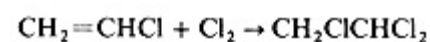
Methyl chloroform (1,1,1-trichloroethane) from vinyl chloride using vinylidene chloride (1,1-dichloroethylene) as an intermediate [11]:



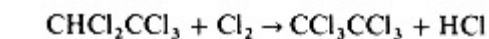
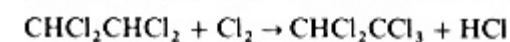
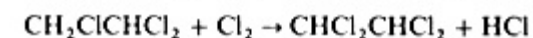
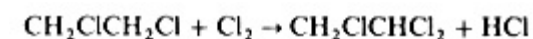
Methyl chloroform from vinyl chloride using ethylidene chloride (1,1-dichloroethane) as an intermediate [37]:



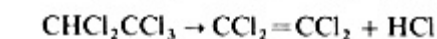
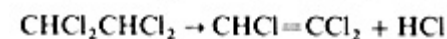
1,1,2-Trichloroethane from vinyl chloride [156]:



Perchloroethylene and trichloroethylene from ethylene dichloride. Starting with ethylene dichloride, 1,1,2-trichloroethane, tetrachloroethane, pentachloroethane, and hexachloroethane are obtained by successive substitutive chlorination:



These chlorides can in turn be dehydrochlorinated to form vinylidene chloride, trichloroethylene, and perchloroethylene:



A commercial process incorporating all of the above reactions for producing perchloroethylene and trichloroethylene has been developed by PPG Industries [78, 88].

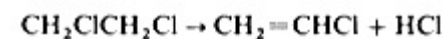
Carried out under pressure and at about 430°C, the oxychlorination and dehydrochlorination reactions take place simultaneously in a multitube fluid bed reactor to facilitate heat removal and temperature control. Good yield (85 to 90%) and high product purity (99.9 + wt.% for both perchloroethylene and trichloroethylene) are reported. See Fig. 11 for the process flow sheet [78].

Other processing schemes are available elsewhere [10, 74].

Dehydrochlorination of Alkyl Chlorides

Some dehydrochlorination reactions of industrial importance are as follows.

Vinyl chloride from ethylene dichloride:



Perchloroethylene from pentachloroethane:



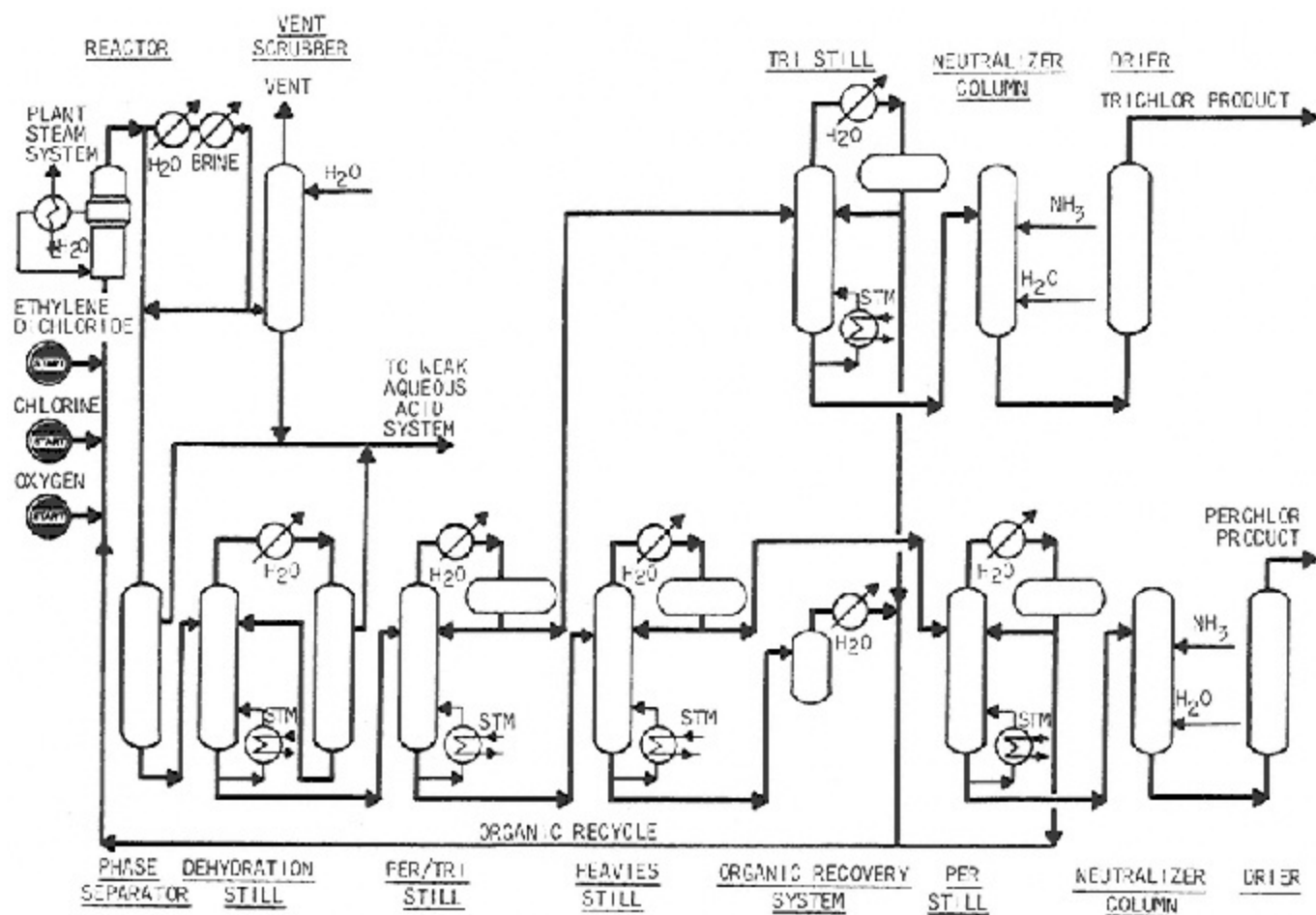
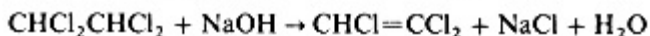


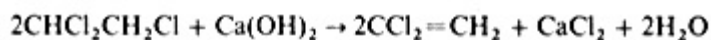
Fig. 11.

Flow sheet for an oxychlorination/oxyhydrochlorination process to produce perchloroethylene and trichloroethylene.
(From Hydrocarbon Processing [78] with permission.)

Trichloroethylene from 1,1,2,2-tetrachloroethane:



Vinylidene chloride from 1,1,2-trichloroethane:



Of these, the dehydrochlorination of ethylene dichloride to produce vinyl chloride is practiced most extensively [37, 7678] and will be discussed below.

Ethylene dichloride (EDC), usually from additive chlorination and/or oxychlorination of ethylene, is cracked thermally. Oftentimes the feed is purified beforehand to remove low boiling and high boiling impurities which impede cracking and enhance by-product formation [4]. Oxygen and chlorine in the feed promote the pyrolysis rate, but their use can also lead to greater by product formation.

Dehydrochlorination is carried out at various pressures up to 25 kPa and at temperatures ranging from 450 to 550°C Ethylene dichloride is fed to a furnace which houses alloy reactor tubes. The furnace is generally direct-fired using either gas or oil as fuel. The reactions which take place during pyrolysis are complex. Temperature, feed composition (including impurities), and surface/volume ratio all affect the rate and the course of the reactions. Good control of this operation is essential and is the subject of three publications [12, 96, 97].

Conversion is usually limited to 50 to 70% per pass in order to minimize coking or carbon deposition in the tubes.

The exit gases from the furnace are cooled quickly in a quench tower. Into the quench tower is also fed a recycle stream which is the crude condensation products from the furnace (mostly EDC). By direct contact, the superheat of the effluent gases is recovered. These gases at their dew point are then condensed in a conventional heat exchanger. Subsequently, fractional distillation is utilized to obtain high-purity vinyl chloride, hydrogen chloride, and ethylene dichloride.

If the dehydrochlorination is carried out at a high pressure (e.g., 250 kPa), the entire effluent stream from the furnace can be liquefied at about 0°C and then fed to a train of distillation column for separation and purification [4].

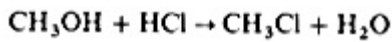
From this product recovery step, HCl is recycled to the oxychlorination reactor and unconverted EDC is recycled back to the furnace. An example of the processing scheme (without the recycle stream for the quench tower) is shown in Fig. 9.

Hydrochlorination of Alcohols

Several alkyl chlorides are produced commercially by hydrochlorinating alcohols. Two of

these are described.

Methyl chloride from methanol:

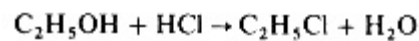


Hydrochlorination of methanol can be carried out by both vapor-phase and liquid-phase processes. For the liquid-phase reaction, hydrochloric acid reacts with alcohol at a reflux temperature (100 to 150°C) in the presence of catalysts such as zinc chloride, aluminum chloride, and bismuth oxychloride [160]. For the vapor-phase reaction at 280 to 350°C, a number of fluidized and fixed-bed catalysts are used. These include alumina gel, Cu_2Cl_2 and ZnCl_2 on pumice, and H_3PO_4 on active carbon. The selectivity with alumina catalyst is about 95 wt%. for both methanol and hydrochloric acid [37, 84].

Sometimes this hydrochlorination is coupled with substitutive chlorination of methane in a combined process for producing chloromethanes. Thus the hydrochloric acid by-produced from the substitutive chlorination step can be utilized in hydrochlorination.

Two commercial processes, belonging to Vulcan Materials Co. and Stauffer Chemical Co., have been summarized in Hydrocarbon Processing [77, 78].

Ethyl chloride from ethanol:



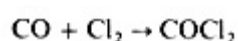
Catalyzed by zinc chloride, ethanol and hydrochloric acid react at 110 to 145°C under reflux condition in a jacketed, glass-lined vessel [51]. Ethyl chloride and water are continuously distilled off as they are formed. The effluent from the reactor is scrubbed with water to remove the free acid. High purity ethyl chloride (99%) is produced in a yield of 95 to 98% based on ethanol. Although this process is simple and clean, it cannot compete economically with hydrochlorination of ethylene [11].

Chlorination of Carbon Monoxide

Phosgene (carbonyl chloride) owes its importance as a raw material for the manufacture of diisocyanates (which in turn are used to produce polyurethanes), pesticides, and polycarbonate resins [11]. As a chlorinating agent, phosgene is used to convert chloroacetic acid to chloroacetyl chloride [64] and niobium oxychloride to niobium pentachloride [62].

Phosgene is an extremely toxic gas. Stringent safety practices, therefore, must be observed in its manufacture, handling, and use. Generally, this poisonous gas is produced and consumed in close proximity.

Phosgene is made by reacting carbon monoxide and chlorine at 200°C over an activated charcoal catalyst.



The feed gases are first dried and filtered separately, and then fed as a mixture to a reactor which is like a shell-and-tube heat exchanger. The catalyst is placed in the tubes. Water is circulated in the shell to remove the heat from this highly exothermic reaction. Iron is an adequate material of construction for the reactor. The yield is about 99%.

The bulk of the phosgene produced is removed from the reactor effluent by condensation. The remainder is scrubbed out of the noncondensable gases in a packed tower using a hydrocarbon solvent. In most cases the reactor effluent containing phosgene is fed directly to other processes. Product recovery, therefore, is not necessary [51].

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Chlorinated Solvents

J. I. Jordan, Jr.

The chlorinated hydrocarbons have been members of our family of chemical compounds for well over a century. Faraday first formed perchloroethylene by the thermal decomposition of hexachloroethane in 1821. We are indebted to such scientists as Liebig, who in 1831 treated chloral with an alkali to obtain chloroform. In 1835 Dumas and Peligot heated methanol with sulfuric acid and sodium chloride to produce a crude form of methyl chloride. Then in 1839 Regnault synthesized carbon tetrachloride by chlorinating chloroform. One year later he isolated methylene chloride by chlorinating methyl chloride in sunlight. Continued effort resulted in isolating 1,1,1-trichloroethane. It was later in 1864 that Fisher formed trichloroethylene by the reduction of hexachloroethane with hydrogen.

Chloroform was probably the first chlorinated solvent to gain commercial significance. In 1846 the use of this compound was established as a general

anesthetic. By 1860 chloroform was in commercial production. The commercial significance of other chlorinated solvents did not begin to develop until the early 1900s when the process for liquefying chlorine was commercialized. The ability to transport chlorine opened its availability as a raw material in widespread commercial application. The substantial growth that has placed chlorinated solvents in a dominant position in the organic chemical industry has occurred over the last 25 years, paralleling the great expansion that has occurred in the petrochemical field.

Chlorinated solvents are used in two broad areas cleaning applications and chemical intermediates. Methyl chloride, chloroform, and carbon tetrachloride are used primarily as chemical intermediates.

Methyl chloride was first used commercially as a refrigerant. As newer compounds began to replace methyl chloride in this role, its use as an intermediate for the production of lead additives for gasoline allowed it to continue at an increased rate of growth. Use of methyl chloride as an intermediate for tetramethyl lead has declined, but a new application has been developed in the manufacture of silicone resins.

Both chloroform and carbon tetrachloride have been displaced from their earlier uses by the development of more effective and less toxic compounds. In its commercial infancy, chloroform was used as an anesthetic while carbon tetrachloride was used as a general solvent and a fire extinguisher. The bulk of sales for both of these chemicals now lies largely as intermediates in the production of fluorinated hydrocarbons.

Use in cleaning applications has been by far the major contributing factor to the growth rate of chlorinated solvents, specifically perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride. The demand for decreasing the cost of degreasing operations, emphasis on protecting the environment, and increased concern for workers' safety have all made major contributions to the increased application of chlorinated solvents in cleaning applications.

Methylene chloride made its initial entry into the solvent field as a paint stripper. Earlier methods of stripping paint from metal surfaces were highly labor-intensive. As the cost of labor increased, the use of methylene chloride became economically more attractive. Once in large-scale production, this solvent has found a most diversified pattern of usage. It is currently employed in the manufacture of photographic film, fibers, and in more recent years aerosol propellants.

Perchloroethylene finds its greatest use in the dry cleaning of clothes and textiles. However, its use as an intermediate in the manufacture of fluorocarbons and metal cleaning also affects market demand. Use of perchloroethylene in fabric cleaning is a good example of utilizing the physical properties of the solvent in a reclamation process permitting the recovery of and subsequent reuse in the cleaning operation.

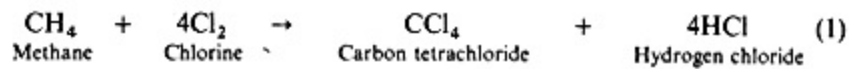
Trichloroethylene is used almost exclusively for the cleaning of metal surfaces. In recent

years the use of trichloroethylene in vapor degreasing operations has come under very close scrutiny by environmental agencies. In the United States there are both state and local environmental laws restricting the level of emission for trichloroethylene. As a result, the demand for this solvent has been declining. It is interesting to note that it has been replaced by

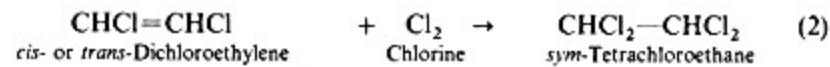
other chlorinated solvents, mainly 1,1,1-trichloroethane, and to a lesser extent perchloroethylene.

The use of 1,1,1-trichloroethane was hampered for a number of years because of poor product stability. Once an adequate stabilization system was developed, this product began to enjoy a relatively rapid rate of growth. Because of its high solvency action and low toxicity, it has gained wide use in replacement of other flammable and more toxic cleaning compounds. Beginning basically as a cold degreasing solvent, its recent growth has accelerated in the area of vapor degreasing because it does not face the ecological problem that is involved in the use of trichloroethylene.

The major chemical reactions used in the various manufacturing processes for chlorinated solvents involve chlorination, hydrochlorination, dehydrochlorination, and oxychlorination. The chlorination reaction involves either the substitution or addition of chlorine into the hydrocarbon molecule. An example of substitution is the reaction of chlorine with methane:



This is a highly exothermic reaction that is normally carried out in a noncatalytic vapor-phase chlorination reactor. An example of addition is the reaction of chlorine with an unsaturated hydrocarbon:

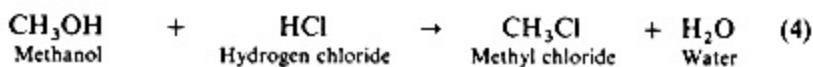


This type of reaction is normally carried out in the liquid phase with or without the use of a catalyst.

Chlorine may also be added to the hydrocarbon molecule by using hydrogen chloride in a hydrochlorination reaction:



In this case hydrogen chloride is reacted with an unsaturated hydrocarbon in the presence of a catalyst. Hydrogen chloride will also react with alcohol to form a chlorinated derivative responding to the alcohol that is used. For example, methyl chloride is produced using methanol:



Dehydrochlorination is the reverse procedure that results in splitting out hydrogen chloride from the chlorinated hydrocarbon molecule. This can be done by treating the chlorocarbon with a strong alkali such as caustic soda, in which case the dissociated chlorine atom is converted to the metal chloride. Commercially, the dehydrochlorination reaction is normally carried out by the use of thermal energy to split out hydrogen

chloride, producing the correspond-

ing unsaturated chlorocarbon. For example, trichloroethylene is obtained by cracking sym-tetrachloroethane:



In chlorination processes, considerable quantities of hydrogen chloride are formed as a by-product. The ability to utilize this hydrogen chloride can have a marked effect on the economics of producing chlorinated solvents. This has led to the application of oxychlorination technology. The first effort to recover chlorine from hydrogen chloride was made using the Deacon reaction where hydrogen chloride and an oxidant in the form of either air or oxygen are passed over a copper chloride catalyst. This process has been commercialized but has not been applied on a wide-scale commercial basis. Of more significance has been the oxychlorination of ethylene utilizing the by-product hydrogen chloride to produce 1,2-dichloroethane from ethylene. The application of oxychlorination technology to the direct manufacture of chlorinated solvents has been slow in developing. At least one commercial unit is in operation producing perchloroethylene and trichloroethylene by oxychlorination. The discovery of more effective catalyst systems and the development of more basic technology in reaction mechanisms should lead to a greater application of oxychlorination in the chlorinated solvents industry.

Even though the technology for producing chlorinated solvents has been commercialized for well over one hundred years, the field still represents a challenge to the development engineer. The growth of chlorinated solvents will to a significant degree rely on the development of new and improved processes capable of utilizing hydrocarbon feedstocks from sources other than natural gas and liquefied petroleum gases. The competitive processes of the future will also be capable of utilizing energy with maximum efficiency and will provide practical solutions to environmental problems relating to the proper containment and utilization of waste streams.

Chloroethanes

J.I. Jordan, Jr.

Introduction

The commercial production of the chlorinated derivatives of ethane has always represented a technical challenge to the development engineer. The challenge lies mainly in the complexity of the chemical reactions involved and the variety of approaches that are available for their manufacture. With processes for the

production of chlorinated methane derivatives, the complexity is limited by the relatively small number of potential products. Most of the commercial chlorinated compounds produced from C₃ hydrocarbons generally employ a high-temperature perchlorination approach where once again the number of end products is limited. On the other hand, the engineer developing a system for producing chloroethanes may be dealing with 15 or more compounds. Since it is normally desirable to limit the net production to one or two compounds, the engineer is faced with complex reactor design problems usually followed by product separation and recovery problems. The complexity of the potential reactions is depicted in Fig. 1.

The purpose of this article is to summarize the current status of technology for the production of chloroethanes and to assist the engineer in identifying some of the major design problems.

Summary of Compounds

The chloroethanes are the saturated derivatives of ethane. However, since the olefinic derivatives are often involved, they are included in the listing of compounds found in Table 1.

Focusing on the saturated derivatives, there is only one compound that has achieved commercial significance as an end product, 1,1,1-trichloroethane, also referred to as methylchloroform. The production of this compound will be the major emphasis of this article. Other derivatives will be discussed as they become involved as intermediates in the production of 1,1,1-trichloroethane.

Commercial Applications

Before proceeding to a discussion of 1,1,1-trichloroethane, a brief summary will be made of the uses for chloroethanes as intermediates for the production of other compounds.

Ethyl chloride became commercially significant as an intermediate for the production of tetraethyl lead used as a gasoline additive. Its uses as an anesthetic and refrigerant produced very little market demand. The fate of lead additives in gasoline will have a significant effect on the future of ethyl chloride.

Ethylene dichloride (1,2-dichloroethane) is used almost exclusively as an intermediate in the production of vinyl chloride. In earlier days it was used in the manufacture of ethylene glycol until replaced by other processes such as the route through ethylene chlorohydrin and the direct oxidation of ethylene. Other applications include use in compounding with tetraethyl lead as an antiknock mixture and as a raw material for the production of ethylenediamine, perchloroethylene, carbon tetrachloride, and trichloroethylene.

As an intermediate, 1,1,2-trichloroethane is used in the manufacture of

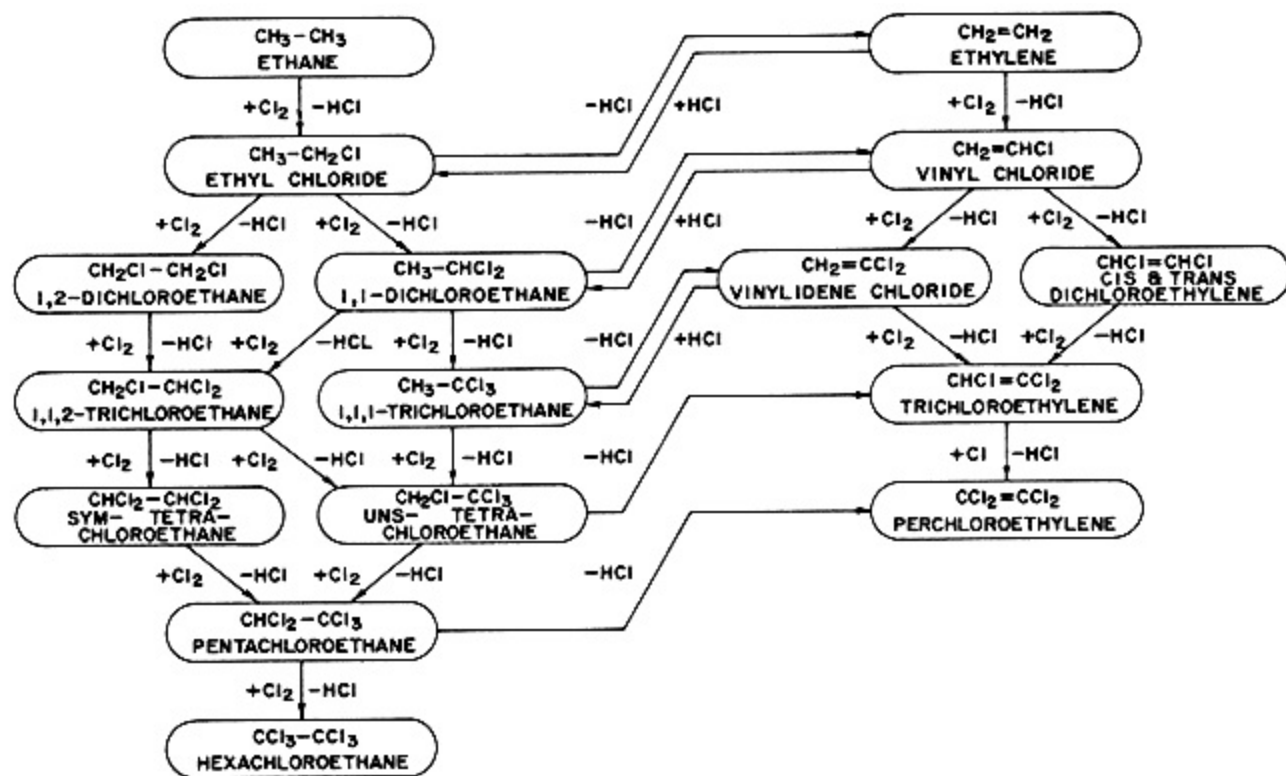


Fig. 1.
Reaction of ethane, ethylene, and their chlorinated derivatives

TABLE 1 Summary of Major Compounds Involved in the Production of Chloroethanes
Compound

Saturated	Unsaturated	Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	Heat of Formation (ΔH_f (gas) at 25°C, kcal/g-mol) [1, 2]
	Ethylene	$\text{CH}_2=\text{CH}_2$	28.05	-103.7	-169.2	+12.49
Ethane		CH_3CH_3	30.07	-88.6	-172	-20.24
Hydrogen chloride		HCl	36.47	-85	-111	-22.063
	Vinyl chloride	$\text{CH}_2=\text{CHCl}$	62.50	-12	-160	+8.5
Ethyl chloride		$\text{CH}_3\text{CH}_2\text{Cl}$	64.52	13	-139	26.81
	Vinylidene chloride	$\text{CH}_2=\text{CCl}_2$	96.95	31.6		+0.58
	trans-Dichloroethylene	$\text{CHCl}=\text{CHCl}$	96.95	48.4	-50	+1.47
1,1-Dichloroethane		CH_3CHCl_2	98.97	57.3	-96.7	-30.93
	cis-Dichloroethylene	$\text{CHCl}=\text{CHCl}$	96.95	60.3	-80.5	+0.90
1,1,1-Trichloroethane		CH_3CCl_3	133.42	74.1		-31.1a
1,2-Dichloroethane		$\text{CH}_2\text{ClCH}_2\text{Cl}$	98.97	83.7	-35.3	-31.02
	Trichloroethylene	$\text{CHCl}=\text{CCl}_2$	131.40	87.2	-73	-1.86
1,1,2-Trichloroethane		$\text{CH}_2\text{ClCHCl}_2$	133.42	113.5	-36.7	-33.94
	Perchloroethylene	$\text{CCl}_2=\text{CCl}_2$	165.85	120.8	-19	-2.9
unsym-Tetrachloroethane		$\text{CCl}_3\text{CH}_2\text{Cl}$	167.86	129		
sym-Tetrachloroethane		$\text{CHCl}_2\text{CHCl}_2$	167.86	146.3	-36	-35.7
Pentachloroethane		$\text{CHCl}_2\text{CCl}_3$	202.31	162	-22	
Hexachloroethane		CCl_3CCl_3	236.76	185.5b		-33.9

aEstimated value.

bAt 77 mmHg pressure.

vinylidene chloride. It may also serve as feed to perchlorination reactions for the production of carbon tetrachloride and perchloroethylene.

Although of waning significance, the tetrachloroethanes have been used as intermediates for the production of trichloroethylene much the same way that pentachloroethane was used for producing perchloroethylene.

The accelerated market for 1,1,1-trichloroethane must be attributed to its use as a degreasing agent. With the development of improved product stabilizer systems, it has penetrated the vapor degreasing field for cleaning of machinery products varying from electric motor parts to intricate turbine rotors. Environmental problems attributed to trichloroethylene have helped to vault 1,1,1-trichloroethane into a prominent position in the chlorinated solvents field.

Stabilized 1,1,1-trichloroethane is also used in cold cleaning operations. Dip, wipe, and spray cleaning are used for removal of waxes, oils, tars, greases, and adhesives. An aerosol grade is also produced for use as a vapor pressure depressant and as a carrier solvent for other materials present in the aerosol formulation.

Other uses of 1,1,1-trichloroethane include:

Intermediate for fluorocarbon production

Solvent for film cleaning

Additive in adhesive formulations and drain cleaners

Coolant for metal-cutting oils

Manufacture of 1,1,1-Trichloroethane

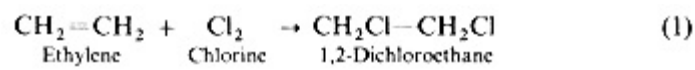
Basically, 1,1,1-trichloroethane can be produced starting with any C₂ hydrocarbon that is either nonchlorinated or has substituted chlorine atoms on the same carbon atom. This would include ethane, ethyl chloride, and 1,1-dichloroethane. A preparatory step must be used with unsaturated compounds, such as ethylene and vinyl chloride, to eliminate the double bond while still maintaining all chlorine atoms on the same carbon atom. This is normally accomplished through hydrochlorination using hydrogen chloride. Vinylidene chloride may also be treated by hydrochlorination, resulting in the direct production of 1,1,1-trichloroethane.

Feed Preparation by Hydrochlorination

Ethylene and vinyl chloride may be hydrochlorinated with hydrogen chloride in preparation for subsequent chlorine substitution needed for the production of 1,1,1-trichloroethane. Under no conditions will direct chlorination of either ethylene or vinyl chloride yield the desired product or useful intermediate [3]. Under moderate chlorination conditions with reaction temperatures below 150°C, the addition of chlorine to the double

bond predominates, resulting in

the formation of a compound with chlorine atoms on adjacent carbon atoms as shown by



As the reaction temperature is increased, substitution of chlorine atoms into the molecule begins to increase as shown by



Further chlorination of vinyl chloride will result in the formation of higher chlorinated olefinics.

The addition of hydrogen chloride across the double bond of olefinic C₂ hydrocarbons is a commercially established process. Although some results have been reported using a vapor-phase reaction promoted by a platinum-aluminum oxide catalyst [4], the bulk of the published data involves a liquid-phase reaction utilizing either ferric chloride or aluminum chloride as a catalyst. As with so many chemical reactions, maximum conversions are achieved with efficient mixing and dispersion of the reactants. This may be accomplished in the liquid-phase reactor by injection of the reactants into the eye of a properly designed agitator. This method not only assures mixing of the reactants, but also serves to keep active catalyst well dispersed throughout the reaction zone.

The development engineer should be alerted to the problems that moisture can create in hydrochlorination systems. Metal surfaces are subject to the corrosive effect of water and hydrogen chloride. The reaction of water with inorganic chlorides results in catalyst deactivation. Every effort should be made to keep hydrochlorination systems totally anhydrous.

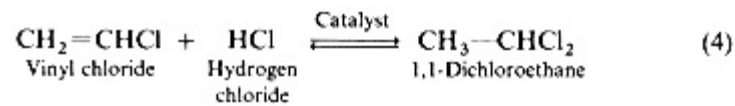
For the production of ethyl chloride, ethylene and hydrogen chloride are sparged into a liquid body containing from 1 to 6% catalyst [3, 6]. The reaction proceeds according to



The liquid is made up primarily of ethyl chloride that is held close to its boiling point, allowing the exothermic heat of reaction to be partially removed by vaporization of the product. With gaseous reactants the heat of reaction at 25°C amounts to about 31,000 Btu/lb · mol of gaseous ethyl chloride formed. A small liquid purge is generally taken from the reactor for removal of heavy by-products and spent catalyst.

Normally hydrogen chloride is fed in excess, but with recovery and recycle of the unreacted hydrogen chloride, yields from both reactants are reported in excess of 98% [5, 6].

The hydrochlorination of vinyl chloride is conducted in much the same manner. The reaction proceeds according to



Either reactant may be fed in excess, but because of the ease in separating hydrogen chloride from the reactor product, hydrogen chloride is generally used in excess over the stoichiometric quantity varying from 1% [7] to 70% [8]. Lower concentrations of vinyl chloride should tend to reduce by-product formation.

The reaction is promoted by the use of a Friedel-Crafts catalyst such as ferric chloride or aluminum chloride although consumption of the iron salt is noted to be considerably lower [9]. Consumption of catalyst would be caused by reduction of catalytic activity resulting from the reaction of the metal chloride with an organic compound. The hydrochlorination of vinyl chloride is normally carried out in the liquid phase. The catalyst is suspended in a liquid body made up primarily of 1,1-dichloroethane. The reactants are sparged into the reaction zone which, as previously mentioned, should be well agitated. The product can be withdrawn as either a vapor or a liquid.

Withdrawal of the product as a liquid increases the amount of heat that must be removed from the reactor to maintain temperature control. One approach uses circulation of the liquid contained in the reactor through an external heat exchanger to maintain the temperature between 38 and 65°C [10]. With gaseous feeds in essentially stoichiometric quantities at 25°C, approximately 42,900 Btu's must be removed for each pound mole of liquid 1,1-dichloroethane formed to maintain the reactor temperature at 50°C.

An alternate method for temperature control could utilize cooling coils in an agitated reactor. This would avoid the maintenance problems associated with pumping the reactor liquid containing catalyst.

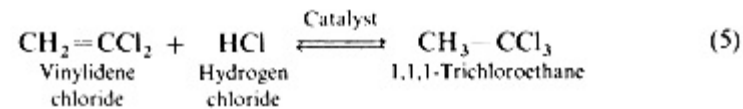
The liquid that is withdrawn from the reactor obviously contains catalyst that must be removed. One system feeds the liquid to a still that is heated to 107°C [11]. The 1,1-dichloroethane is withdrawn as a vapor and subsequently recovered by condensation. Uncondensed hydrogen chloride and vinyl chloride can be recycled to the hydrochlorinator.

Withdrawal of the product as a vapor will require higher reactor temperatures at a given pressure in order to maintain the reaction mass at its boiling point. An excess of hydrogen chloride would reduce the required temperature by reducing the partial pressure of the product in the vapor. Starting with a gaseous feed mixture at 25°C containing a 20% molar excess of hydrogen chloride, approximately 29,600 Btu's must be removed for each pound mole of 1,1-dichloroethane formed to maintain a reactor temperature of 60°C. With the vapor draw, spent catalyst and heavy by-products could be removed through a small liquid purge.

Conversion of vinyl chloride to 1,1-dichloroethane in liquid-phase reactors is normally quite high. A 99.6% conversion has been reported using less than 1%

excess hydrogen chloride in a liquid-phase reactor maintained at 30°C [7]. Again a 99.0% vinyl chloride conversion was obtained with a little over 70% excess hydrogen chloride [8].

The hydrochlorination of vinylidene chloride for the direct production of 1,1,1-trichloroethane again follows the same general processing involved in producing ethyl chloride and 1,1-dichloroethane. The reaction with hydrogen chloride takes place according to the following overall equation:



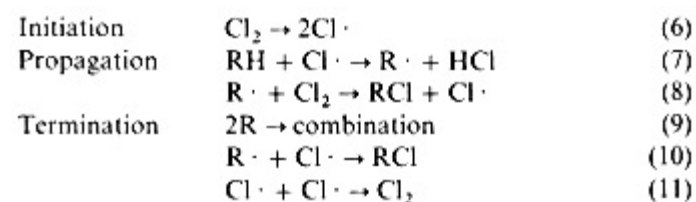
The reactants in essentially equal molar quantities are introduced into a liquid body made up primarily of 1,1,1-trichloroethane and containing 0.3% ferric chloride [12]. The reaction may be conducted under vacuum to hold the reactor temperature below 60°C. At atmospheric pressure the reactor must be held at about 74°C, the normal boiling point of 1,1,1-trichloroethane. The reactant mixture consists of 1.048 mol of hydrogen chloride per mole of vinylidene chloride. From the liquid-phase reaction mass, 0.947 mol of 1,1,1-trichloroethane per mole of vinylidene chloride fed are withdrawn as a vapor.

The reaction products must be further treated for removal of unreacted vinylidene chloride and hydrogen chloride.

Chlorination for the Production of 1,1,1-Trichloroethane

Ethane, ethyl chloride, and 1,1-dichloroethane are all potential feedstocks for the production of 1,1,1-trichloroethane by chlorination.

Before proceeding to specific processes, a general discussion of hydrocarbon chlorination might be helpful. The chlorination of hydrocarbons is thought to proceed via the following equations [13, 14]:



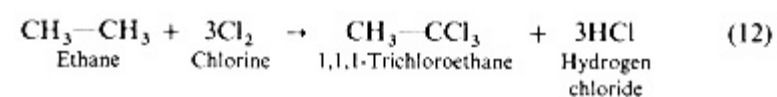
The initiation step shown in Eq. (6) may be promoted by the catalytic effect of reactor surfaces although the reaction can be supported by thermal dissociation of the chlorine molecule [15]. It is also thought that light used in photochemical processes activates the dissociation [16]. This is supported by the fact that propagation in the photochemical chlorination of C₂ hydrocarbons proceeds at much lower temperatures than in thermal systems.

For thermal chlorination the difficulty in predicting the distribution of chlorinated

derivatives lies in the complex mechanism that is simplified in Eqs. (7)

and (8). Earlier theories stated that during vapor-phase chlorination the substitution of a chlorine atom onto a carbon atom would hinder further substitution on that carbon atom [15]. As will be shown, however, commercial experience supports the conclusion that in thermal chlorination of C₂ hydrocarbons there is a high degree of selectivity toward chlorine substitution onto the same carbon atom. The relative rates of hydrogen abstraction (Eq. 7) do support the theory that the α -hydrogens of ethyl chloride and 1,1-dichloroethane are more reactive than the β -hydrogens, but the difference in reactivity is not great enough to account for the high selectivity to 1,1,1-trichloroethane [17]. The inability to predict product distribution at varying reactor conditions leaves reactor design in an empirical state that is dependent on specific data developed through actual experience.

One important point should be made with regard to reactor design for thermal chlorinators. From the heats of formation of the reactants and products involved in C₂ hydrocarbon chlorination, it is readily apparent that the reactions are highly exothermic. The reaction of ethane and chlorine to form trichloroethane is



With gaseous reactants and products, the heat of reaction at 25°C is approximately 138,700 Btu/lb-mol of 1,1,1-trichloroethane formed. Since this reaction is normally carried out in a reaction zone from 370 to 430°C, some of the liberated energy is taken out as sensible heat in the products. For an example, consider a strictly hypothetical case involving the single reaction in Eq. 12 with essentially complete conversion of the reactants. Approximately 33,200 Btu/lb-mol of 1,1,1-trichloroethane would be removed from the reaction zone as sensible heat in the effluent gases at 400°C. Then 105,500 Btu/lb-mol of 1,1,1-trichloroethane would have to be removed if the reaction temperature is to be controlled at 400°C.

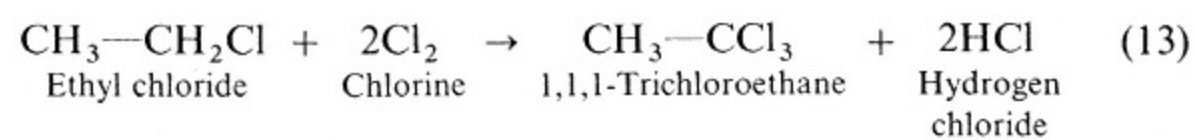
Without an effective heat removal system, the reactor temperature would quickly exceed the limit that is necessary to maintain product stability. At temperatures in excess of 480°C, the formation of decomposition products such as carbon will become a dominant factor.

Temperature control within the reaction zone can be controlled in several manners.

1. Use of fluid bed reactor. Patent literature reports the use of fluid bed reactors for the chlorination of mixtures of ethyl chloride and 1,1-dichloroethane [18]. This type of technology has been applied to many exothermic reactions. Normally, internal cooling coils are employed to transfer heat from the circulating bed of solids to a heat transfer medium carried inside the coils. This facilitates the recovery of energy released during the reaction in the form of thermal energy that can be conveniently recovered as steam.

2. Use of excess reactants. The heat of reaction can be removed through the

sensible heat of effluent gases if sufficient unreacted feeds are available. This can involve the use of excess hydrocarbon feed to avoid the processing difficulties associated with the presence of unreacted chlorine in the effluent. In the chlorination of ethyl chloride to produce 1,1,1-trichloroethane, a sufficient excess of ethyl chloride may be used to control reactor temperatures. As a hypothetical case, consider the energy balance involved with the overall reaction



With gaseous reactants and products, the heat of reaction at 25°C is approximately 87,100 Btu/lb-mol of 1,1,1-trichloroethane. The energy removed with the sensible heat in the products at 400°C is approximately 28,600 Btu/lb-mol of product. Using an average specific heat for ethyl chloride of 18.5 Btu/lb-mol °F, the remaining 58,500 Btu's can be removed with approximately 4.68 mol of ethyl chloride per pound mole of 1,1,1-trichloroethane. The feed mixture would then contain 2.84 mol of ethyl chloride per mole of chlorine to be reacted.

The problem involved with the use of excess reactants is that recovery of products in the effluent is complicated by dilution with lower boiling reactants such as ethyl chloride. However, this approach should be considered by the design engineer as a viable means of controlling reaction temperature.

3. Use of inert diluent. Perhaps a more acceptable method for temperature control that is compatible with ethane or ethyl chloride chlorination is found in the use of diluents. It has been suggested that hydrogen chloride may be recycled to the reactor to act as a diluent [19]. Although the reactions involved in C₂ hydrocarbon chlorination may include a hydrochlorination reaction that would be favored by an excess of hydrogen chloride, it is doubtful that this reaction would be of any significance in thermal reactors operating between 370 and 430°C. The recycle of hydrogen chloride would be beneficial in its action as an inert to carry the heat of reaction from the reaction zone through sensible heat. Since the specific heat of gaseous hydrogen chloride is low relative to the organic constituents, a significant recycle of hydrogen chloride would be involved that must be dealt with in the downstream recovery system.

4. Recycle of intermediates. A high conversion of either ethane or ethyl chloride to 1,1,1-trichloroethane is difficult to achieve on a once-through basis. Normally, underchlorinated intermediates such as ethyl chloride and 1,1-dichloroethane will be present in the reactor effluent and can be recycled after recovery in a downstream separation system. As will be discussed, ethylene and vinyl chloride will also be present in the thermal chlorinator effluent. When subjected to the preparatory hydrochlorination step to eliminate double bonding between carbon atoms, the saturated compounds that are produced can also be recycled to assist in reactor temperature control and increase the yield of 1,1,1-

trichloroethane from the incoming raw materials.

In summary on the point of temperature control, the design engineer must carefully consider the calculation of the energy balance around the reactor. This is important for maintenance of a controlled reaction maximizing raw material yields to the desired product. Selection of the method of control will also affect design of the downstream recovery system.

Finally, in discussing the general concept of thermal chlorination, it should be noted that the mixing of reactants can have a significant effect on reactor performance. Methods of introducing reactants into the reaction zone are rarely discussed in publications, mainly because of the proprietary nature of these developments. One study showed that product distribution from the chlorination of ethane could be effected by the use of multiple injection of chlorine along a longitudinal-type reactor [20]. The reduction in unsaturated compounds could be explained by the improved mixing that was obtained with the increase in the number of injection points.

The problem of reactant mixing becomes more acute as the ratio of chlorine to carbon in the feed mixture is increased. Poor mixing increases the possibility of creating high chlorine concentrations in the reaction zone a problem that is accelerated as the chlorine content of the feed is increased. Mixing in liquid phase reactions is important to obtain good raw material conversions, but in thermal chlorination the presence of localized high concentrations of chlorine will promote product degradation as evidenced by the formation of carbon. To reduce the quantity of unreacted feeds that must be recovered, it is desirable to maintain a reasonable per-pass conversion of reactants which requires increased chlorine concentration in the feed and therefore increases the significance of reactant mixing.

Chlorination of Ethane

The development of a process for the production of 1,1,1-trichloroethane by the direct chlorination of ethane has been reported [10], and at least one commercial system is in operation utilizing this approach.

In the ethane chlorination process, chlorine and ethane are injected into a reaction zone maintained between 370 and 480°C. A superficial residence time of about 15 s is provided to insure that the conversion of chlorine is complete. Product distribution is controlled by the ratio of chlorine to ethane in the feed mixture the higher the ratio, the higher the formation of polychlorinated ethanes over monochlorinated derivatives.

As was previously discussed, the thermal chlorination of ethane is marked with a surprising selectivity to compounds containing chlorine substituted on the α -carbon of the ethane molecule. Thus the major reaction products include, in addition to ethyl chloride, 1,1-dichloroethane and 1,1,1-trichloroethane. The only other chlorinated derivative present in significant concentrations is vinyl chloride. The ethyl chloride and 1,1-dichloroethane can be recycled to the reactor. To maximize the yield of 1,1,1-trichloroethane, the vinyl chloride can be hydrochlorinated to produce additional 1,1-

dichloroethane and combined with the recycle to the reactor. It then becomes a matter of adjusting the chlorine-to-ethane ratio to provide the quantity of underchlorinated in-

TABLE 2 Thermal Chlorination of Ethane, Example 1 [10]

Compound	Composition (mol/mol of Cl ₂ fed)		
	Feed	Effluent	Net Produced
Vinyl chloride		0.175	a
Ethyl chloride	0.105	0.112	0.007
Vinylidene chloride		0.062	0.062
1,1-Dichloroethane	0.669	0.494	
1,1,1-Trichloroethane		0.189	0.189
1,2-Dichloroethane		0.010	0.010
1,1,2-Trichloroethane		0.012	0.012
Miscellaneous		0.007	0.007

aThe 0.175 mol of vinyl chloride are used to produce 1,1-dichloroethane by hydrochlorination with hydrogen chloride to make up for the amount consumed in the thermal reaction.

intermediates required for temperature control in the thermal reactor and to obtain the desired distribution of compounds withdrawn as net products.

Under so-called "balanced" conditions which are intended to maximize the production of 1,1,1-trichloroethane, results have been reported feeding 0.441 mol of ethane per mole of chlorine in addition to ethyl chloride and 1,1-dichloroethane as shown in Table 2 [10].

Further enhancement of the yield to 1,1,1-trichloroethane can be obtained by feeding the vinylidene chloride to the same hydrochlorination unit that is used for the conversion of vinyl chloride to 1,1-dichloroethane.

The product distribution can be significantly altered by reducing the feed ratio of chlorine to ethane. The product distribution of organics obtained when feeding 0.599 mol of ethane per mole of chlorine with ethyl chloride and 1,1-dichloroethane is shown in Table 3 [10]. In this case 1,1-dichloroethane production is essentially balanced in the thermal unit, eliminating the necessity for hydrochlorination. Vinyl chloride would be withdrawn as a coproduct.

TABLE 3 Thermal Chlorination of Ethane, Example 3 [10]

	Composition (mol/mol of Cl ₂ fed)		
	Feed	Effluent	Net Produced
Vinyl chloride		0.120	0.120
Ethyl chloride	0.313	0.315	0.002
Vinylidene chloride		0.023	0.023
1,2-Dichloroethylenes		0.001	0.001
1,1-Dichloroethane	0.582	0.606	0.024
1,1,1-Trichloroethane		0.124	0.124
1,2-Dichloroethane		0.013	0.013
1,1,2-Trichloroethane		0.004	0.004

Chlorination of Ethyl Chloride

Chlorination of ethyl chloride to produce 1,1,1-trichloroethane may be carried out in the vapor phase thermally or photochemically.

Published data for the photochemical system given in Table 4 show the sensitivity of product distribution to the feed composition [21].

As noted in Table 4, hydrogen chloride is used as a diluent for reactor temperature control in conjunction with heat transfer from the outside surface of the reactor. The relatively low reactor temperature required by photochlorination is advantageous from the point of product stability as evidenced by the absence of unsaturated compounds formed by dehydrochlorination at higher temperatures. The predominance of chlorine substitution on the α -carbon does suffer with the subsequent increase in the formation of 1,1,2-trichloroethane relative to 1,1,1-trichloroethane.

Thermal chlorination of ethyl chloride proceeds in a manner similar to ethane. The results of ethyl chloride chlorination are given in Table 5 [22].

In addition to the RCl products, ethylene amounting to about 20.6% of the ethyl chloride fed is also produced. As with ethane chlorination, the net product distribution can be altered by changing the ratio of ethyl chloride to chlorine in the feed. The net production of vinyl chloride can be eliminated by using hydrochlorination for conversion to 1,1-dichloroethane which is recycled to the reactor.

The application of fluid-bed technology to the chlorination of ethyl chloride has been reported [18]. The fluidizing medium was a fine iron-free sand through which the feed gases were passed at a rate to maintain a preferred superficial velocity of 1 to 2 ft/s. In one example, a linear velocity of 1.5 ft/s was used. The results are given in Table 6.

TABLE 4 Photochlorination of Ethyl Chloride

	Table 2 [21]	
	Line 1	Line 2
Feed (mol/mol Cl ₂ fed)		
Ethyl chloride	0.455	0.303
Hydrogen chloride (diluent)	0.909	0.606
Reactor temperature (°C)	50	50
Retention time (s)	7.8	7.8
RCl product composition (wt. %)		
1,1-Dichloroethane	10.0	1.4
1,1,1-Trichloroethane	66.0	54.0
1,2-Dichloroethane	8.2	3.6
1,1,2-Trichloroethane	14.8	21.6
Tetrachloroethanes	1.0	13.4
Pentachloroethane	0.0	4.4
Hexachloroethane	0.0	1.6

TABLE 5 Thermal Chlorination of Ethyl Chloride

Run 21B [22]

Feed (mol/mol Cl ₂ fed)	
Ethyl chloride	0.622
1,1-Dichloroethane	0.538
Reactor temperature (°C)	389399
Composition of RCI's in effluent (wt.%)	
Vinyl chloride	15.4
Ethyl chloride	1.8
Vinylidene chloride	12.8
Dichloroethylenes	4.1
1,1-Dichloroethane	20.8
1,1,1-Trichloroethane	39.7
1,2-Dichloroethane	0.9
Trichloroethylene	0.7
1,1,2-Trichloroethane	2.2
Other	1.6

Unreacted 1,1-dichloroethane is recovered and recycled to the reactor to maximize the yield of 1,1,1-trichloroethane.

One rather interesting report dealing with chlorination of ethyl chloride gave data showing extremely high conversions of ethyl chloride and 1,1-dichloroethane to unsaturates [19]. In two reported runs with varying feed compositions, the RCI product contained 91.8 and 60.4% of unsaturated compounds, mainly vinyl chloride and vinylidene chloride. The total effluent from the chlorinator was fed to a hydrochlorination system for conversion to 1,1,1-trichloroethane and other saturated C₂ derivatives, such as 1,1-dichloroethane for recycle to the chlorinator. Reactor temperatures ranged from 345 to

TABLE 6 Chlorination of Ethyl Chloride in a Fluid Bed Reactor

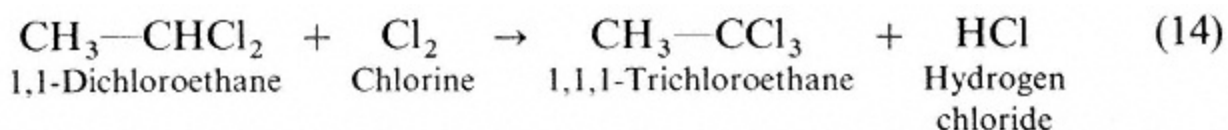
Example 1 [18]

Feed (mol/mol Cl ₂)	
Ethyl chloride	0.683
1,1-Dichloroethane	1.001
Temperature (°C)	427
Pressure (lb/in. 2gauge)	70
Product analysis (wt.%)	
1,1-Dichloroethane	21.0
1,1,1-Trichloroethane	31.8
1,2-Dichloroethane and 1,1,2-trichloroethane	2.7
Vinyl chloride and vinylidene chloride	12.0
Hydrogen chloride	32.5

429°C which would not explain the predominance of unsaturated products that would be caused by dehydrochlorination at high temperatures. It is noted that the data were collected from the operation of a relatively small nickel reactor with an inside diameter of 0.81 in. and a length of 51 in. Wall effects from this high surface to volume metal reactor may have played a part in altering the reaction mechanism to favor the formation of unsaturates. Past experience has shown that the chlorination reaction with hydrocarbons is subject to wall effects. A marked induction period was required to initiate the reaction using a clean glass reactor as compared to one on which carbonaceous materials had been deposited [15].

Chlorination of 1, 1-Dichloroethane

The process for the chlorination of 1,1-dichloroethane to 1,1,1-trichloroethane does not involve the severe temperature control problem associated with lesser chlorinated feedstocks. Using a gas-phase reaction shown in Eq. (14), the heat of reaction at 25°C is calculated to be about 40,000 Btu/lb-mol of 1,1,1-trichloroethane:



This is in sharp contrast to the heat of reaction involved with ethane chlorination. Normally an excess of 1,1-dichloroethane can be used to control the temperature in the reactor during the chlorination reaction.

Photochlorination techniques in both the vapor phase and liquid phase have been applied to the chlorination of 1,1-dichloroethane. According to the published results, selectivities to 1,1,1-trichloroethane are relatively high in these systems. Results from vapor-phase photochlorination are given in Table 7 [23].

The reactor temperature was controlled by cooling water passing through a jacket incorporated into the reactor design. It will be noted that the selectivity to 1,1,1-trichloroethane is much less sensitive to the feed composition which is such an important factor in both ethane and ethyl chloride chlorinations.

Liquid-phase photochlorination obviously involves much lower reaction temperatures as compared to vapor phase. This reduces the selectivity of the reaction to α -carbon substitution, resulting in an increase in the production of 1,1,2-trichloroethane relative to 1,1,1-trichloroethane. One reported result [24] using 0.26 parts by weight of 1,1-dichloroethane to 0.19 parts of chlorine in a photochemical reactor maintained at 36°C showed that the reaction products contained 75% by weight of 1,1,1-trichloroethane and 25% by weight of 1,1,2-trichloroethane.

The use of solvents such as carbon disulfide have been tested on the theory that the presence of a selective agent can inhibit chlorine substitution on the β -carbon. Under

conditions identical to the above example, 0.12 parts by weight of 1,1-dichloroethane and 0.12 parts of carbon disulfide were mixed with 0.21

TABLE 7 Vapor-Phase Photochlorination of 1,1-Dichloroethane

	Example 1 [23]	
	Test No. 4	Test No. 6
Feed (mol/mol Cl ₂ fed)		
1,1-Dichloroethane	1.673	0.249
Reaction temperature (°C)		
Inlet	60	60
Maximum	150	150
Conversion (mol%)		
1,1-Dichloroethane	23.8	91.1
Selectivity (mol% formed from converted 1,1-dichloroethane)		
1,1,1-Trichloroethane	86.6	84.4
1,1,2-Trichloroethane	12.3	7.2
unsym-Tetrachloroethane	0.8	5.8
sym-Tetrachloroethane	0.3	1.7
Pentachloroethane	0.0	1.0

parts of chlorine. The reaction product was reported to contain 90% 1,1,1-trichloroethane and 10% 1,1,2-trichloroethane [24].

Straight vapor-phase thermal chlorination of 1,1-dichloroethane would have the advantage of simplifying the reactor design as compared to photochlorinators. However, the higher temperatures required by thermal chlorination increase the rate of dehydrochlorination relative to chlorine substitution, resulting in the production of unsaturated derivatives, mainly vinyl chloride and vinylidene chloride.

Alternate Methods for Production of 1,1,1-Trichloroethane

Before leaving the summary of processes that the design engineer should consider for the production of 1,1,1-trichloroethane, one alternate method will be discussed. This method involves the production of 1,1,2-trichloroethane that is subsequently dehydrochlorinated to produce vinylidene chloride. This unsaturated C₂ compound can then be converted to 1,1,1-trichloroethane by hydrochlorination as previously discussed.

A liquid-phase reaction as shown in Eq. (15) may be used for the production of 1,1,2-trichloroethane from ethylene and chlorine [25]. The reported results from such a system were collected from a liquid-phase reactor containing a liquid mixture of 1,2-dichloroethane and 1,1,2-trichloroethane with 0.006 wt.% ferric chloride. Table 8 summarizes the results.

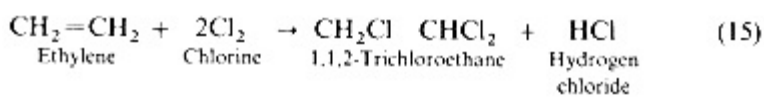


TABLE 8 Liquid-Phase Chlorination for the Production of 1,1,2-Trichloroethane

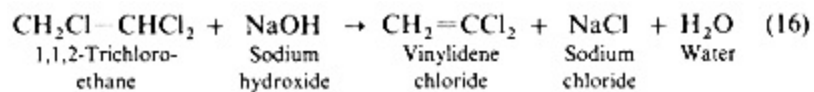
Example 1 [25]

Feed (mol/mol Cl ₂ fed)	
Ethylene	0.501
Reactor temperature (°C)	116
Pressure (lb/in. 2gauge)	22
Production (mol/mol Cl ₂ fed)	
1,2-Dichloroethane	0.001
1,1,2-Trichloroethane	0.482
Tetrachloroethanes	0.032
Pentachloroethane	0.015

The conversion of ethylene to 1,1,2-trichloroethane is 96.2% while the chlorine conversion is 96.5%. The 1,1,2-trichloroethane is separated by standard distillation techniques.

The reactor temperature is maintained by using the heat of reaction to vaporize a portion of the liquid in the reactor. The vapors are cooled to 32°C and the condensate is returned to the reactor.

The next step in this process for the production of 1,1,1-trichloroethane involves the conversion of 1,1,2-trichloroethane to vinylidene chloride. One of the simplest approaches treats 1,1,2-trichloroethane with a strong base [12]. In this case the base is supplied through an aqueous solution of sodium hydroxide typical of the composition of cell liquor from a diaphragm chlorine cell 10.5 wt.% sodium hydroxide and 19.5 wt.% sodium chloride. The overall reaction proceeds according to



A packed tower is provided with heat supplied by the injection of steam at the bottom. The aqueous base containing 0.160 lb-mol/h of sodium hydroxide is fed along with 0.145 lb-mol/h of 1,1,2-trichloroethane. The temperature varies from 115°C in the bottom of the tower to 33°C at the top. Product vinylidene chloride is withdrawn overhead at a rate of 0.139 lb-mol/h that results in a yield from 1,1,2-trichloroethane of 95.4%.

Although the yield of vinylidene chloride from 1,1,2-trichloroethane by treatment with a strong base is relatively high, the recovery of chlorine is low because 1 mol of sodium chloride is produced for each mole of product. For this reason work has been reported on the development of a thermal dehydrochlorination process [26]. In this work, 1,1,2-trichloroethane was vaporized and mixed with nitrogen in equal molar quantities with a small amount of chlorine. The mixture was passed through a reactor packed with 6 to 8 mesh rock salt and heated to 450°C. Essentially complete conversion of the

1,1,2-trichloroethane was obtained, yielding a mixture of 50-50 mol% vinylidene chloride and cis- and trans-dichloroethylene.

The next step for the production of 1,1,1-trichloroethane involves the hydrochlorination of vinylidene chloride as has previously been discussed. This is a rather straightforward process when essentially pure vinylidene chloride is used as the organic feed constituent. Using the thermal dehydrochlorination approach, the recovery of the cis- and trans-dichloroethylene isomers is involved. In the previously mentioned reference [26] the mixture of dichloroethylenes is fed to a hydrochlorination reactor along with a stoichiometric amount of hydrogen chloride. A conversion of 82% of theoretical was obtained, resulting in equal molar quantities of 1,1,1-trichloroethane and 1,1,2-trichloroethane. The latter was recycled to the thermal dehydrochlorination step following product separation.

Product Recovery

The discussion up to this point has been centered in the reactions involved in the production of 1,1,1-trichloroethane.

In systems using vapor-phase reactions, the first step in the recovery step is to remove the sensible heat from the vapors and to at least partially condense the effluent. This may be accomplished in a quench step where the vapor effluent is countercurrently scrubbed with a cool liquid in a tower with several contact stages [10]. Overhead vapors are further cooled in a water-cooled heat exchanger where partial condensation occurs. A portion of the condensate is returned to the quench tower to serve as the scrubbing liquid. This system is obviously nothing more than a rectifying section of a standard distillation tower with the superheat in the reactor effluent supplying the boilup. This design can be used as part of the product purification system in removing higher boiling compounds.

In the system just described, the thermal energy contained in the reactor effluent is discharged to a cooling tower. Now that the recovery of energy is being emphasized along with product recovery, the design engineer should consider alternate systems that would provide for the recovery of thermal energy. This would be an obvious advantage of fluid-bed reactors. To elaborate on this point, in a thermal chlorination system utilizing excess reactants, inert diluents, or recycle systems for reactor temperature control, the heat of reaction is removed as sensible heat in the reactor effluent gases. Recovery of this energy must be designed into the subsequent quench step. In a fluid-bed reactor equipped with internal cooling coils, a significant portion of the heat of reaction can be removed from the reaction zone by vaporization of condensate that is used as a coolant inside the coils. Generation of steam represents a direct approach to energy recovery that is an integral part of the reactor design.

Following the quench step, the reactor products are separated into components. In many processes, hydrogen chloride is normally recovered first. The cooled effluent that would

consist of vapor and liquid streams is introduced

into a distillation tower equipped with a reboiler and a refrigerated overhead partial condenser [10]. The temperature of the refrigerant in the overhead partial condenser is controlled to condense hydrogen chloride that is returned to the tower as reflux. The overhead product vapor can be withdrawn as essentially pure hydrogen chloride. In cases of ethane and ethyl chloride chlorinations, ethylene will also be present in addition to unreacted ethane in the former case.

For the design of a hydrogen chloride stripping tower, calculation techniques for multicomponent distillation may be employed using hydrogen chloride as the light key and the next lighter boiling component, such as vinyl chloride, as the heavy key. In the absence of specific data, the calculations may be based on the assumption of ideality using component vapor pressures to determine vapor-liquid equilibrium concentrations. If the assumption of ideality is to represent a good approximation, mixtures of organics and hydrogen chloride must be miscible. This is particularly true in the rectifying section of the tower where high concentrations of hydrogen chloride are encountered in the liquid phase. The dielectric constant for liquid hydrogen chloride is close to the range for most chlorinated hydrocarbons. This means that in an anhydrous condition the hydrogen chloride molecule is covalent, which would support the assumption of miscibility.

In the stripping section of the tower, the assumption of ideality is subject to more question since temperatures are normally above the 51.4°C critical temperature of hydrogen chloride. Actual vapor-liquid equilibrium data on the specific system involved are obviously the soundest basis for design.

Another method of recovery uses compression of the gases containing the hydrogen chloride [12]. The gases are simultaneously cooled to - 35°C and compressed to 200 lb/in. 2gauge. Further purification is obtained by scrubbing the chilled hydrogen chloride with a stream of high boiling liquid organics.

Subsequent separation of the chlorinated organic constituents in the reactor effluent is dependent upon the chlorination process. The separation may involve a wide range of C₂ chlorinated derivatives, varying from the low boiling vinyl chloride to the higher boiling compounds such as 1,1,2-trichloroethane and the tetrachloroethanes. Fortunately for the design engineer, there are not a significant number of pitfalls involved in the separation of components from mixtures of these chlorinated hydrocarbons.

Formation of azeotropes is not significant although there are exceptions that should be noted. Table 9 summarizes the reported azeotropes among chlorinated hydrocarbons [27].

Carbon tetrachloride would be present by virtue of C₁ contaminants in the hydrocarbon feed to a chlorination reaction. Its presence would create a problem in the purification of 1,1,1-trichloroethane because of the very narrow spread in boiling points between the two compounds carbon tetrachloride 76.8°C and 1,1,1-trichloroethane 74.1°C.

Except for one binary mixture that will be discussed later, reasonable relative volatilities exist between binaries that are involved as key components in the separation of chlorinated C₂ mixtures. This can be shown by the data presented in Table 10 [28] that give relative volatilities at the extremes of concentrations.

TABLE 9 Azeotropes in Binary Mixtures of Chlorinated Hydrocarbons

Mixture	Normal Boiling Point (°C)	Boiling Point (°C)	Azeotrope	
			Concentrations of Light Com- ponent (wt.%)	
Carbon tetrachloride	76.8	75.3	78.4	
1,2-Dichloroethane	83.7			
1,2-Dichloroethane	83.7	82.1	56.5	
Trichloroethylene	87.2			
1,1,2-Trichloroethane	113.5	112	43	
Perchloroethylene	120.8			

The relative volatility is defined by

$$\alpha = \frac{Y_1(1 - X_1)}{X_1(1 - Y_1)} \quad (17)$$

where = vapor concentration of light component,
Y₁ mole fraction

X₁ = liquid concentration of light component,
mole fraction

α = relative volatility

The relative volatility data of Table 10 supports the presence of an azeotrope between 1,2-dichloroethane and trichloroethylene.

With reasonable values of relative volatilities, most mixtures of chloroethanes can readily be separated by conventional distillation except for the binary 1,1,1-trichloroethane and 1,2-dichloroethane. As the concentration of 1,1,1-trichloroethane approaches 100 mol%, the volatility relative to 1,2-dichloroethane is further reduced to 1.065 [27].

TABLE 10 Relative Volatility of Binary Mixtures

Components in Mixture		Relative Volatility, Liquid Composition of Component (mol%)	
Light Component	Heavy Component	5.0	95.0
Vinyl chloride	Ethyl chloride	1.885	2.252
Ethyl chloride	Vinylidene chloride	1.790	1.847
Vinylidene chloride	1,1-Dichloroethane	2.355	2.100
1,1-Dichloroethane	1,1,1-Trichloroethane	1.707	1.593
1,1,1-Trichloroethane	1,2-Dichloroethane	1.530	1.087
1,2-Dichloroethane	Trichloroethylene	1.403	0.850

Because of the difficulty in separating 1,1,1-trichloroethane from 1,2-dichloroethane by conventional distillation, extractive distillation systems have been developed. With this approach an extractant is used to increase the relative volatility between the two chloroethanes. Data using different extractants are shown in Table 11 [29].

A two-tower system is required for extractive distillation. In the first tower the extractant is fed at some point above the 1,1,1-trichloroethane-1,2-dichloroethane feed. The separation between the two chloroethane compounds is primarily carried out in the section between these two feed points. The top section removes the extractant from the 1,1,1-trichloroethane that passes overhead where it is condensed. A portion of the condensate is returned to the tower as reflux.

The bottom section of the tower is used to strip 1,1,1-trichloroethane away from the extractant-1,2-dichloroethane mixture. Boilup is supplied by a steam heated reboiler.

The second tower is used to strip 1,2-dichloroethane away from the extractant which is recovered and recycled to the first tower. This would be a conventional distillation step with the difficulty of separation dependent upon the boiling point of the extractant used. It is obvious that essentially all of the 1,2-dichloroethane must be removed from the extractant since the concentration of this impurity in the recycle to the first tower would have a significant effect on the efficiency of separation required to produce a pure 1,1,1-trichloroethane product.

Product Stabilization of 1,1,1-Trichloroethane [30]

Chlorinated hydrocarbons are known to decompose when exposed to moisture, light, air, heat, and metal surfaces. These decompositions can be caused by hydrolysis, oxidation, and metal or metal-salt catalyzed dehydrochlorination. All of these decomposition mechanisms result in the formation of hydrogen chloride which establishes a corrosive environment. The saturated chlorinated hydrocarbons, such as carbon tetrachloride, chloroform, ethylene dichloride, and 1,1,1-trichloroethane, as a group are subject to hydrolysis and oxidation as mechanisms for decomposition. Of these compounds, 1,1,1-trichloroethane is less susceptible to oxidation and therefore presents less of a problem in this respect. The unsaturated chlorinated hydrocarbons, trichloroethylene and perchloroethylene, are sensitive to oxidation and undergo decomposition in the presence of air, light, and heat. Trichloroethylene is particularly vulnerable to this mechanism of decomposition.

The product 1,1,1-trichloroethane undergoes hydrolysis in the presence of moisture. It is especially susceptible to metal or metal chloride catalyzed dehydrochlorination. The autocatalytic and rapidly progressive decomposition forms hydrogen chloride. Although 1,1,1-trichloroethane is not very sensitive to oxidation, some of the major components employed as stabilizers are quite easily oxidized, and an antioxidant is very helpful in vapor degreasing

TABLE 11 Extractive Distillation Separation of 1,1,1-Trichloroethane and 1,2-Dichloroethane

Table 1 [29]

	Extractant	Liquid Phase Composition (wt.%)		Relative Volatility ^a	Pressure (mmHg)
		1,1,1-Trichloro- ethane	1,2-Dichloro- ethane		
None		96.80	3.20	1.10	727.6
Epichlorohydrin	42.79	54.43	2.78	1.68	711.5
n-Butyronitrile	67.18	30.62	2.20	2.33	717.3
Tetrahydrofurfuryl alcohol	25.72	73.33	0.95	1.37	723.0
Anisole	59.96	39.09	0.95	1.50	
Isobutyl acetate	57.22	40.30	2.48	1.56	727.2
Nitroethane	61.13	36.74	2.13	1.99	722.7
1-Nitropropane	71.04	26.96	2.00	1.66	720.7
Epichlorohydrin- isobutylacetate	33.0229.81	34.80	2.37	1.64	716.3

^aVolatility of 1,1,1-trichloroethane relative to 1,2-dichloroethane

operations to retard peroxide formation. The peroxides formed are known to react with 1,1,1-trichloroethane, resulting in corrosive conditions.

Prior to 1957, 1,1,1-trichloroethane had minor usage because stabilizer systems which were adequate for trichloroethylene and perchloroethylene were only partially effective with 1,1,1-trichloroethane. Its use was limited to cold cleaning applications of nonaluminum-containing metals. Glass or galvanized containers were used for storage to obtain reasonable shelf life. In 1957, 1,4-dioxane was reported to be effective as a stabilizer for 1,1,1-trichloroethane in contact with aluminum. A nonprimary alkanol was added to permit its storage in plain steel containers without discoloration. This was the first stabilizer system developed specifically for 1,1,1-trichloroethane.

Today there are over 200 active United States patents dealing with the stabilization of chlorinated hydrocarbons. Most of these patents cover stabilizer systems for 1,1,1-trichloroethane.

Although it is difficult to describe the action of various stabilizer components, it is believed that they can be characterized by the following properties: (1) preventing or retarding oxidation, (2) chelating of metal ions, (3) scavenging of hydrogen chloride, and (4) pacifying metal surfaces

Many classes of compounds have been developed for use as stabilizers for chlorinated hydrocarbons in general and for 1,1,1-trichloroethane in particular. Some of these classes and specific compounds are given in Table 12. Selection of the proper combination of chemicals for stabilization and their concentrations depend upon the end use of the product. As has previously been outlined, major end uses include the following: (1) vapor degreasing, (2) cold cleaning, (3) aerosol formulations, (4) intermediate for fluorocarbon production, (5) film cleaning, and (6) specialty uses.

TABLE 12 Classes and Specific Compounds Used for Stabilization of 1,1,1-Trichloroethane

Class	Compound
Cyclic ethers	1,4-Dioxane, 1,3-dioxolane
Organic oxides	Butylene oxide, epichlorohydrin
Ketones	Methyl ethyl ketone
Alcohols	sec-Butyl alcohol, isobutyl alcohol
Esters	Ethyl acetate
Acetylenic alcohols	Methyl butynol
Nitriles	Acrylonitrile, β -ethoxypropionitrile
Amines	Diallylamine, diisopropylamine
Oximes	Acetaldoxime
Nitroalkanes	Nitromethane, nitroethane
Morpholines	N-Methylmorpholine
Pyrroles	N-Methylpyrrole
Alkylphenols	tert-Amylphenol, thymol
Polyphenols	Hydroquinone monomethyl ether
Acetals	Methylal
Glycol ethers	Ethylene glycol mono and dialkyl ethers

Vapor degreasing grades of 1,1,1-trichloroethane contain from 3 to 7 wt.% of stabilizers and additives. The major chemicals used include nitromethane, 1,3-dioxolane, 1,4-dioxane, butylene oxide, sec-butyl alcohol, isobutyl alcohol, N-methyl pyrrole, and toluene. Some of these chemicals perform more than one function in stabilizing 1,1,1-trichloroethane, and synergistic effects have been noted.

Cold cleaning grades of 1,1,1-trichloroethane are not stabilized as heavily as the vapor degreasing grades, but the systems employed are usually very similar.

Aerosol grades of 1,1,1-trichloroethane that are employed in various aerosol formulations utilize stabilizers containing such compounds as dioxane, isobutyl alcohol, sec-butyl alcohol, butylene oxide, and methylal.

For fluorocarbon production, the intermediate 1,1,1-trichloroethane is a high purity product with a very low stabilizer content in the range of 0.05 to 0.10% butylene oxide.

Film cleaning is a specialized use for 1,1,1-trichloroethane, and the product formulated for this application employs a low concentration of alcohol alone as the stabilizer.

For the other specialty uses of 1,1,1-trichloroethane, the stabilizer formulation is usually modified depending upon the manufacturer's requirements.

In the selection of chemicals for the stabilization of 1,1,1-trichloroethane, the performance of the stabilizer system is the prime factor. Other factors involved in the selection of a system include the following: (1) cost and availability of the chemical components, (2) toxicity, (3) boiling range of the component, (4) formation of azeotropes, (5) odor, (6) stability of the chemical in the presence of air and water as well as thermal stability, and (7) potential carcinogenicity.

Selection of a Process for Producing Chloroethanes

Many factors are involved in selecting a process for the manufacture of any product, and this is the case for chloroethanes. No attempt will be made to outline all the factors involved with chloroethanes, but two will be mentioned because they have profound effects on the ultimate process selection.

Chlorine Balance

The selectivity of chlorine conversion to the desired product must be of prime consideration in comparing processes for the manufacture of chloroethanes. In most of the techniques that have been discussed, chlorine that is not recovered in the organic product is converted mainly to hydrogen chloride. On a weight basis the ratio of hydrogen chloride (anhydrous basis) to organic product can vary from nil to well over 1.0. As the ratio increases, the value of

hydrogen chloride becomes more of an economic factor. Chlorine content of this by-product must be recovered by marketing as an end product or as an intermediate for the production of other chlorinated compounds. The development of oxychlorination has made the latter approach a viable alternative. The most significant oxychlorination process practiced today is for the conversion of hydrogen chloride and ethylene to 1,2-dichloroethane. This compound is widely used as an intermediate for the production of vinyl chloride that, in addition to its value in the production of polyvinyl chloride, can be used for feed to a chloroethanes unit as has previously been discussed. In short, the selection of a chloroethanes process is very much contingent on the type of manufacturing complex into which the plant is to be integrated for maximizing the utilization of chlorine.

Hydrocarbon Source

Finally, the selection of a chloroethanes process must be influenced by the availability of hydrocarbon feedstocks. The conventional processes start with either ethane or ethylene. The development engineer responsible for making the process selection must know what hydrocarbon source is available to him on the plant site.

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Chlorohydrins

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The word "chlorohydrin" has attained common technical usage to denote various chemical compounds which contain both a chloro and a hydroxyl group. A major review article covers the chemistry of the compounds [1], and the word has limited appearance in recent volumes of Chemical Abstracts. It is omitted as a general term from chemical dictionaries [2]. Commonly, the term is not applied to aromatics, such as the chlorophenols, and so such compounds are not included in the following discussion.

The word usually is taken to mean compounds in which the chloro and hydroxyl groups are vicinal. These may often be dehydrochlorinated to give oxirane linkages. However, other aliphatic compounds also are called "chlorohydrins," and the term may logically embrace alicyclic compounds also. The word also may be defined as embracing compounds which are part of the larger class of halohydrins. However, such compounds incorporating bromine, etc., are less important industrially than the chlorohydrins. The fluoroalcohols also are of less interest in this context because their chemistry is not specific to the reactions connoted by the term halohydrins.

The subject is therefore defined for present purposes as "organic compounds with aliphatic or alicyclic linkages which contain one or more chlorine atoms and hydroxyl groups."

The presence of two functional groups which have different reactivities at times makes this class of compounds useful for the synthesis of end products which are technically hard to make, or uneconomic, by other means. The most common use of the group is for dehydrochlorination to produce an oxirane (epoxide) ring or to form larger rings. Also reactions involving the hydroxyl group (esterification, etc.) or the chloro moiety (Williamson reaction), etc., are frequently used.

Survey of the worldwide literature indicates a broad area of research, product development, and process study in connection with this class of bifunctional compounds. Preliminary surveys of the area show many hundreds of references to a wide variety of both simple and complex compounds. The chemistry of the compounds is diverse. Their proposed uses are many. It has been necessary to restrict the following discussion to some of the simpler compounds of the class. Those that are included have (1) known commercial importance, (2) some apparent commercial potential, or (3) some illustrative interest. Naturally, it is not always possible to assess the objective or the commercial feasibility of patented subject matter.

The economic disadvantage of the chlorohydrins for commercial use has heretofore lain in (1) the loss of chlorine as HCl when HOCl was used as the chlorohydroxylating medium,

and (2) the material loss occurring when chlorine is eliminated by dehydrochlorination, coupling, and hydrolysis. Efforts to

overcome (1) are indicated in the patent literature.

The examples which are the most prominent technologically and commercially are ethylene, propylene, glycerol chlorohydrins, and epichlorohydrin. (The latter is not strictly a chlorohydrin by the above definition, but is included because of its common name and its relevance as an intermediate in the manufacture of glycerol.) These compounds for complete discussion, in their function as intermediates to produce the analogous epoxides and glycols, are referred to under the appropriate headings (cf. ethylene oxide and glycol, propylene oxide and glycol, glycerol). Their inclusion below is illustrative, since their technology is the best-developed of their class.

Conventionally, much of the commercial interest has been in the ability of the vicinal chlorohydrins to form epoxides. Understandably, the commercial technology of the products lacks detailed disclosure, and selection of the items for discussion must be largely judgmental. For conditions leading to the manufacture of less commercially important chlorohydrins it is necessary to be guided by analogy or by literature which is largely of Eastern origin.

Chemical Abstracts has been taken as an adequate index for this field of applied chemistry. From references to it, the reader may make his basic selection of sources related to his particular area of interest. Some judgment must be exercised as to the technological merit or applicability of disclosures in the literature.

It is customary to select literature disclosures which show good practical yields or technological data. This study covers such a wide range that many procedures can be taken only as preliminary, and judgment must be exerted as to their technical value. Not all material which is of value, doubtless, has been included. Generally speaking, it has not been possible to test the referenced material for its practical value (patents, research papers).

A general word is necessary regarding the impact of changing conditions on the technical use of the chlorohydrins. This study has been made difficult by the extremely variable economic situation with respect to raw material (hydrocarbon) and energy availability, and the situation with respect to the environmental impact of the process effluents. In more settled times it is easy judgmentally to exclude certain technology because of obvious economic barriers. Perhaps we are not justified in being so peremptory today. Thus a few years ago epoxides might be made by processes that were less selective chemically but had lower energy requirements. Today the higher selectivity might pay for greater energy input, if environmental factors were tolerable. Thus each project depends on a specific local balance of cost considerations. This situation is stressed in a recent review article by Myszkowski [3].

In the material below, the trivial name of each compound is given first (if one exists), followed by the "molecular formula." Otherwise, the Chemical Abstracts system of nomenclature is followed. For discussion purposes, the word "chlorohydrin" and other

common terminology is used in order to avoid confusion on the practical level of communication. However, as the use of more precise nomenclature becomes widespread, this practice will become

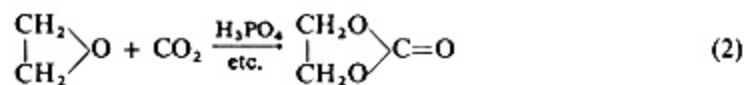
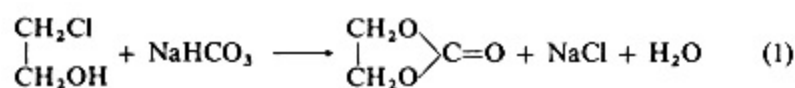
obsolete. Eventually the term "chlorohydrin" will probably drop from the literature.

Historical

The word "chlorohydrin" is the common or "trivial" name for a diverse group of organic compounds that have in common the presence of a chloro and a hydroxyl group in an aliphatic chain. As such, they are a part of the broader class of halohydrins. However, none of the class other than chlorohydrins has attained much industrial significance.

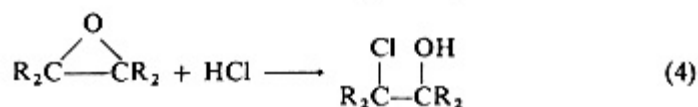
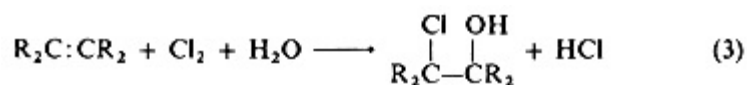
The growth of chlorohydrin technology in the decades 1920-1960 provided large-scale intermediates for the production of oxirane (epoxy) compounds which were used in manufacturing polyhydroxy derivatives (glycols and glycerol). Later in the same period other chemical methods were developed for arriving at the same oxygenated products without the use of chlorine in intermediate steps, and by 1970 these seemed to have won the field, except under conditions where special economic or technical considerations kept the chlorine-based processes in the running.

Many products which were prepared through chlorohydrins now can be more economically prepared by the use of oxiranes (epoxides) without the attendant loss of the chlorine group. For example, in the case of ethylene carbonate:



Reaction (2) would be the commercial route today.

Thus many reactions which were common textbook chemistry in the 1950s would today have new technical materials substituted. It is even possible that improved methods of epoxidation via hydroperoxides, peroxides, or direct oxidation may make it economic to reverse the classic route and make chlorohydrins by addition of HCl:



The disposal of dilute HCl solutions has been a bugbear of the hypochlorination route to chlorohydrins in which the concentration is limited (1)

by the solubility of chlorine in water, and (2) by the additive chlorination of olefin and the formation of by-products at high concentrations.

The chemistry of the chlorohydrins has been the subject of several very good textbook review articles [1, 4, 5]. The first of these is primarily a review on ethylene, propylene, trimethylene, and tetramethylene chlorohydrins, glycerol mono- and dichlorohydrins, and epichlorohydrins. The literature review is quite extensive. A more recent review article (in Polish) is very pertinent (see below) [3].

General

Manufacture

Table 1 lists a number of relatively simple chlorohydrins. A few of these are in commercial manufacture. Most of the remainder are referred to in the patent literature, many with indications of potential uses.

Generally speaking, there is not enough physical data given to warrant including these. Where it is given, the boiling point at a specified pressure is indicated, or melting point in the case of high-boiling compounds.

The chemistry of the common 2- to 4-carbon chlorohydrins was included in a study of the formation of epoxides, glycols, and glycerine from the corresponding olefins by the hypochlorination process [6]. The effects of space velocity, concentration, mole ratio, and temperature are given in graphical form, with optima, for the following olefins:

Ethylene

Propylene

2-Butylene

Allyl alcohol

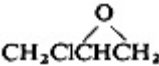
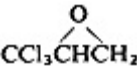
Allyl chloride (liquid and vapor)

The data presented are taken both from the authors' work and from recent publications. Generally, the chlorohydrins are produced in optimum yields of 88 to 93% from the olefins, with 3.5 to 6% dichloro addition product and 0.5 to 2% chloroether formed. The corresponding oxirane compounds (ethylene, propylene, 2-butylene oxides, and epichlorohydrin) are produced in 87 to 92% yield in the presence of lime, with 6 to 11% glycol. In the presence of sodium carbonate, propylene chlorohydrin and epichlorohydrin are converted 94 and 98% to glycol and glycerol, respectively, while when hydrolyzing with combined Na_2CO_3 and NaOH , glycerol dichlorohydrin gives 94% yield to glycerol.

A thorough review of the literature is available from a Polish source [3]. This covers the available information on the formation of chlorohydrins from ethylene, propylene, butenes, butadiene, allyl chloride, allyl alcohol, and methallyl chloride. The variables


covered include rates of reaction, mole ratio

TABLE 1 Names and Structures of Some Simple Chlorohydrins

Compound Name	Class	Formula	Structure	Boiling Point (°C, mm)
Ethylene chlorohydrin				
2-Chloroethanol	Vicinal chlorohydrin	C ₂ H ₅ ClOH	CH ₂ ClCH ₂ OH	128.7
Propylene chlorohydrins				
1-Chloro-2-propanol	Vicinal chlorohydrin	C ₃ H ₇ ClO	CH ₂ ClCH ₂ OHCH ₃	127.0
2-Chloro-1-propanol	Vicinal chlorohydrin	C ₃ H ₇ ClO	CH ₂ OHCHClCH ₃	133
2,3-Dichloro-2-propen-1-ol	Vicinal chlorohydrin	C ₃ H ₄ Cl ₂ O	CHCl: CClCH ₂ OH	80720
Glycerol monochlorohydrins				
3-Chloro-1,2-propanediol (α)	Vicinal chlorohydrin	C ₃ H ₇ ClO ₂	CH ₂ ClCHOHCH ₂ OH	11611
2-Chloro-1,3-propanediol (β)	Vicinal chlorohydrin	C ₃ H ₇ ClO ₂	CH ₂ OHCHClCH ₂ OH	124.5515
Glycerol dichlorohydrins				
2,3-Chloro-1-propanol	Vicinal chlorohydrin	C ₃ H ₆ Cl ₂ O	CH ₂ ClCHClCH ₂ OH	182
1,3-Chloro-2-propanol	Vicinal chlorohydrin	C ₃ H ₆ Cl ₂ O	CH ₂ ClCHOHCH ₂ Cl	175.86.3765
Trimethylene chlorohydrin				
3-Chloro-1-propanol	1,3-Chlorohydrin	C ₃ H ₆ ClO	CH ₂ ClCH ₂ CH ₂ OH	1612
Substituted 1,3-chloropropanols	1,3-Chlorohydrin	Various	CH ₂ ClCH ₂ CH(OH)R	(See Table 6)
Polychloro propanol				
2,2,3,3-Tetrachloro-1-propanol	Vicinal chlorohydrin	C ₃ H ₄ Cl ₄ O	CHCl ₂ CCl ₂ CH ₂ OH	75952 86886
Epichlorohydrin				
Chloromethyl oxirane	Epoxide	C ₃ H ₅ ClO		1324
Trichloro propylene oxide,				
1,1,1-Trichloromethyl oxirane	Epoxide	C ₃ H ₃ Cl ₃ O		
Butylene monochlorohydrins				
1-Chloro-2-butanol	Vicinal chlorohydrin	C ₄ H ₉ ClO	CH ₂ ClCHOHCH ₂ CH ₃	141
2-Chloro-1-butanol	Vicinal chlorohydrin	C ₄ H ₉ ClO	CH ₂ OHCHClCH ₂ CH ₃	74625
3-Chloro-2-butanol	Vicinal chlorohydrin	C ₄ H ₉ ClO	CH ₃ CHClCHOHCH ₃	139
4-Chloro-2-butanol	1,3-Chlorohydrin	C ₄ H ₉ ClO	CH ₂ ClCH ₂ CHOHCH ₃	7013
3-Chloro-1-butanol	1,3-Chlorohydrin	C ₄ H ₉ ClO	CH ₃ CHClCH ₂ CH ₂ OH	13840


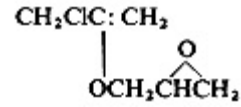
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Compound Name	Class	Formula	Structure	Boiling F (°C, m
4-Chloro-1-butanol, tetramethylene chlorohydrin	ω-Chlorohydrin	C4H9ClO	CH2Cl(CH2)3OH	8451
Isobutylene chlorohydrins				
2-Chloro-2-methyl-1-propanol	Vicinal chlorohydrin	C4H9ClO	CH3CCl(CH3)CH2OH	132.5
1-Chloro-2-methyl-2-propanol	Vicinal chlorohydrin	C4H9ClO	CH2ClC(OH)(CH3)CH3	128
1-Chloro-2-Chloromethyl-2 -propanol	Vicinal chlorohydrin	C4H8Cl2O	(CH2Cl)2C(OH)CH3	174
1,2-Dichloro-2-methyl-3-propanol	Vicinal chlorohydrin	C4H8Cl2O	CH2ClCCl(CH3)CH2OH	180
Butadiene dichlorohydrins				
1,4-Dichloro-2,3-butanediol	Dichlorohydrin	C4H8Cl2O2	CH2ClCHOHCHOHCH2Cl	
1,3-Dichloro-2,4-butanediol	Dichlorohydrin	C4H8Cl2O2	CH2ClCHOHCHClCH2OH	
3,4-Dichloro-1,2-butanediol	Dichlorohydrin	C4H8Cl2O2	CH2ClCHClCHOHCH2OH	
2,3-Dichloro-1,4-butanediol	Dichlorohydrin	C4H8Cl2O2	CH2OHCHClCHClCH2OH	14014
3-Chloro-2-methyl-1,2-propanediol	Vicinal chlorohydrin	C4H9ClO2	CH2ClC(OH) (CH3)CH2OH	801.0
1,3-Dichloro-2-methyl-2- propanol; bis(1-Chloromethyl) ethanol	Vicinal chlorohydrin	C4H6Cl2O	CH3C(OH)(CH2Cl)2	62.81
2-Chloromethyl epichlorohydrin, bis(2- Chloromethyl)oxirane	Epoxide	C4H6Cl2O		7823
Styrene chlorohydrin, 2-Chloro-1-phenylethanol	Vicinal chlorohydrin	C8H9ClO	C6H5CH(OH)CH2Cl	12811
2,3-Dichloro-2-buten-1,4-ol	Unsaturated chlorohydrin	C4H6Cl2O2	2(CH2OHCCl)2:	13614
Chloroether glycols	Vicinal chlorohydrin	Various	(See Table 6)	mp 78
Long-chain chlorohydrins	A. Vicinal chlorohydrins B. ω-Chlorohydrins		Dodecyl, octadecyl, etc. Various	
1,1,1-Trichloro-2-methyl-2- propanol "Chloretane," "chlorobutanol"	Polychloro halohydrin	C4H7Cl3O	CCl3C(OH)(CH3)CH3	167 mp 98.595
Chloral hemiacetals and mercaptals	Polychloro halohydrin	Various	CCl3CH(OH)XR(X=O or S)	
1,1,1,3-Tetrachloro-2-methyl-2- propanol	Polychloro halohydrin	C4H6Cl4O	CCl3C(OH)(CH3)CH2Cl	9511

(continued)

TABLE 1 (continued)

Compound Name	Class	Formula	Structure	Boiling (°C, r
4,4,4,2-Tetrachloro-1-butanol	Polychloro halohydrin	C4H6Cl4O	CCl3CH2CHClCH2OH	841
1,1,2,2-Tetrachloro-3-butanol	Polychloro halohydrin	C4H6Cl4O	CCl2CCl2CH(OH)CH3	991011
4,4,4-Trichloro-1,2-epoxybutane "Trichloro butylene oxide"	Epoxide	C4H5Cl3O		10811. 77782
5,6-Dichloro-1-hexanol	ω-Chlorohydrin	C6H12Cl2O	CH2ClCHCl(CH2)4OH	90911
Chlorofluoro alcohols 1,1,1,3,3- Pentachloro-3-fluoro- 2-propanol	Polyhalo chlorohydrins	Various C3H2Cl5FO	Example: CCl3CH(OH)CCl2F	6945
Diglycol chlorohydrin, 2-(2- chloroethoxy)ethanol	Chloroether alcohol	C4H9ClO2	CH2ClCH2OC2H4OH	196.8
Triglycol chlorohydrin; 2-(2- chloroethoxy)ethoxyethanol	Chloroether alcohol	C6H13ClO3	CH2ClCH2O(CH2)2O(CH2)2OH	
Tetraglycol chlorohydrin (homologous)	Chloroether alcohol	C8H17ClO4	Homologous	1353
Pentaglycol chlorohydrin (homologous)	Chloroether alcohol	C10H21ClO5	Homologous	150153
1-Chloromethylvinyl-1-glycidyl ether	Chloroether epoxide	C6H9ClO2		64662.0
1-Chloro-2-alkoxy-3-propanols	Chloroalcohol ether	Various	CH2ClCH(OR)CH2OH (R=alkyl group)	
Pentaerythritol dichlorohydrins	1,3-Dichlorohydrin	C5H10Cl2O2 C5H10Cl2O2	CH2OHC(CH2Cl)2CH2OH CH2ClC(CH2Cl) (CH2OH)CH2OH	
Mucochloric acid	Carboxy unsaturated chlorohydrin	C4H4Cl2O3	CH2OHCCl: CClCO2H	
1-Chloro-2-butyne-4-ol	Acetylenic chlorohydrin	C4H5ClO	CH2ClC≡CCH2OH	55571
1-Chloro-2-pentyne-4-ol	Acetylenic chlorohydrin	C5H7ClO	CH2ClC≡CCH(OH)CH3	54550.0

temperature, the rate of raw material injection, and solution recycle. The author also correlates the dipole moment of the olefin with reactor capacity. The data are presented in a "regularized" form so as to be suitable for use in process design, and also for extrapolation to analogous reactions. Other publications from the same source indicate further availability of kinetic data and reaction conditions, and olefin solubility [7].

Electrolytic processes have been disclosed mainly in connection with ethylene and propylene chlorohydrins, and are more properly discussed under the corresponding epoxides. Such a process is mentioned in current literature as a commercial potential [8], but no announcement of a production facility has been made. Perhaps changes in the energy versus hydrocarbon supply situation might make such technology economic under future circumstances.

Table 2 presents a general survey of preparative methods which have been recorded for chlorohydrins. Not all of these are of commercial significance. However, they are listed in order to illustrate the varied chemistry which may be applied, and it is not impossible that techniques which are too advanced at the date of writing will be reduced to practice, or that methods which are uneconomic under some circumstances may be usable in others.

A discussion of each method appears under the example of the product which illustrates it. Generally, the simplest case shown in the literature is used. The utility of the method is a matter for the ingenuity of the chemist or engineer, and the economic circumstances of his project.

Table 6 gives other groups of compounds by formula and boiling point, which are listed as additional items in the literature, and which may be useful for reference.

Uses:

General

The chemical reactions of chlorohydrins may involve either or both functional groups (Cl and OH). Certain uses of the compounds themselves (solvents, biological agents, etc.) are suggested by the literature. Many proposed applications are proprietary and their status in commercial use is not necessarily known. The large amount of research effort which has been put into the compounds and the large number of patents issued makes it probable that at least some uses are, or have potential to be, commercial. General applications are listed here.

Oxirane Formation

The formation of an oxirane ring by dehydrochlorination with alkali is a classic use:

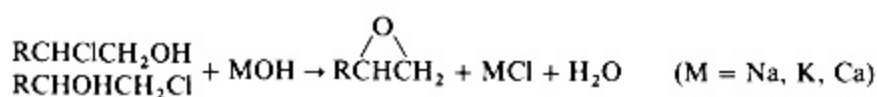


TABLE 2 Type Reactions Used in the Preparation of Chlorohydrins

Reaction Type	Example	Representative Conditions	Yield (%)	Typical Products	Technical Status, 1975	Refs.
I. Hypochlorination (Chlorohydroxylation)						
a. Aqueous Chlorine	i. $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$	Atm pressure; 60°C; 1.5 $\text{MC}_2\text{H}_5/\text{Cl}_2$; 6.4% chlorohydrin	88-89 (on Cl_2)	Ethylene chlorohydrin	Commercial	3, 11
	ii. $\text{CH}_2=\text{CH}_2 + \text{HOCl} \rightarrow \text{CH}_2\text{ClCH}_2\text{OH}$			Propylene chlorohydrin	Commercial	3, 5
b. Hypochlorous Acid	ii. $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{ClCH}_2\text{OH} + \text{HCl}$ $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HOCl} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl}$	Chloride-free aq. 45°C; 30 min	98	Glycerol chlorohydrins Butylene chlorohydrins Propylene chlorohydrins	Commercial Patent Patent	3, 5 3, 5 22
c. Oxy chlorination	i. $\text{C}_2\text{H}_4 + \text{HCl} + \frac{1}{2}\text{TeO}_2 \rightarrow \text{CH}_2\text{ClCH}_2\text{OH} + \frac{1}{2}\text{Te}$	TeO_2 dissolved in aq 20% HCl ; 8 $\text{MC}_2\text{H}_5/\text{TeO}_2$; 100°C; 1-20 atm; regenerate TeO_2	89.5	Long-chain aliphatics Ethylene chlorohydrin	Patent	12
	i. $\text{Te} + \text{O}_2 \rightarrow \text{TeO}_2$			Propylene chlorohydrins	Patent	12
	ii. Oxidative hypochlorination: $\text{C}_4\text{H}_7\text{CH}=\text{CH}_2 + \text{HCl} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl} + \text{H}_2\text{O}$	Second step in hypochlorination to utilize HCl ; 7 h; 75°C low concentration	97%	Propylene chlorohydrin	Patent	22
d. Electrochemical	iii. Other oxidative systems include: $\text{TiCl}_3 + \text{CuCl}_2$; $\text{CuCl}_2 + \text{PdCl}_2 + \text{CaCl}_2$	TiCl_3 suspension dilute aq HCl ; 60°C; 75 atm; 5 h	88-91 (on TiCl_3)	Ethylene chlorohydrin	Patent	14, 15
	Chlorohydrin is formed and dehydrochlorinated to produce the epoxide in an electrolytic cell by electrolysis of NaCl solution.	Aq NaCl 8-9% at 52°C atm, 3.7 V, olefin conversion 18-40%, current eff. 81-82%	81-98% (PO on C_3)	Propylene oxide Ethylene oxide	Patent Patent	27, 28
e. Hypochlorites	i. $\text{CH}_2\text{ClCH}=\text{CH}_2 + (\text{CH}_3)_3\text{COCl} \rightarrow \text{CH}_2\text{ClCH}(\text{OH})\text{CH}_2\text{Cl}$	Batch: 15-20°C; 4 h; 5% DClH max.	94 (on AC)	Glycerol dichlorohydrins	Patent	64
	ii. Inorganic hypochlorites			Tetramethylene chlorohydrin Special cases	 Patent	 58
2. Chlorination						
a. Additive, ethylenic	$\text{CH}_2=\text{CHCH}_2\text{OH} + \text{Cl}_2 \xrightarrow[\text{Et}_2\text{O}]{\text{HCl}}$ $\text{CH}_2\text{ClCHClCH}_2\text{OH}$ (87.7%) $\text{CH}_2\text{ClCH}(\text{OH})\text{CH}_2\text{Cl}$ (11.9%)	Cl_2 in presence of HCl and aliphatic ether	94-98	Glycerol dichlorohydrins	Patent	58
	b. Additive, acetylenic $\text{CH}_3\text{OHC}\equiv\text{CCH}_2\text{OH} + \text{Cl}_2 \xrightarrow[\text{MeOH}]{\text{HCl}}$ $\text{CH}_3\text{OHCCl}_2\text{CCl}_2\text{CH}_2\text{OH}$ $(\text{CH}_3\text{OHCCl}_2\text{CCl}_2\text{CH}_2\text{OH})$	Inert solvent (MeOH); -5 to +10°C (ex: -50°C)	78 (tetra)	Tetrachlorobutane-2,3-diol (dichlorobutane-2,3-diol)	Patent	34, 35

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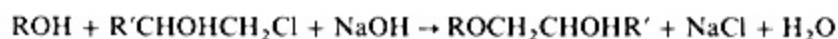
c. Photosynthesis	$\text{CCl}_3\text{OCH}_2\text{XOHCH}_2 + \text{Cl}_2 \xrightarrow[\text{CCl}_4]{\text{UV}}$ $\text{CCl}_3\text{C}(\text{CH}_2)(\text{OH})\text{CH}_2\text{Cl}$	Solvent CCl_4 ; UV irradiation; 65°C max	Distributed	Tetrachloro-2-methyl-2-propanol	Patent	78
d. Substitutive	$\text{CH}_2\text{OHC}\cdot\text{CCH}_2\text{OH} + \text{COCl}_2 \xrightarrow[\text{DMF}]{} \text{CH}_2\text{OHC}\cdot\text{CCH}_2\text{Cl} + \text{CO} + \text{HCl}$	Catalyst: Dimethylformamide; 50–60°C; 8–10 h	60.5%	4-Chloro-butyl-2-ol-1,1,4-Dichlorobutyn-2		40
3. Hydrochlorination						
a. Epoxides	$\text{CH}_2\text{CH}_2 + \text{HCl} \xrightarrow{\text{Me}_3\text{N}}$ $\text{CH}_3\text{OHCH}_2\text{Cl}$	Chlorohydrin solvent; 1 atm, 0–25°C	99	Ethylene chlorohydrin	Patent	13
b. Alcohols	$\text{HO}(\text{CH}_2)_n\text{OH} + \text{HCl} \rightarrow \text{Cl}(\text{CH}_2)_n\text{OH} + \text{H}_2\text{O}$	Reflux at 70–90°C	74–79	Tetramethylene chlorohydrin	Laboratory	41
4. Hydroxylation	$\text{CH}_2\text{CCH}:\text{CH}_2 + \text{H}_2\text{O}_2 \xrightarrow[\text{solution}]{\text{HCO}_2\text{H}}$ $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{OH}$			2 Methyl 3 chloro 1,2-propanediol	Patent	74
5. Alkoxylation	$\text{CH}_2\text{C}(\text{CH}_2\text{OH}) + \text{CH}_3\text{CH}_2 \xrightarrow[\text{H}_2\text{PO}_4]{\text{O}}$ $\text{CH}_2\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_3)_2\text{OH}$ ($\rightarrow \text{CH}_2\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_3)_3\text{OH}$, etc.)	Acid catalysts (ex: H_3PO_4); varying mole ratios, conversions	Varies	Diglycol chlorohydrin, isomers	Laboratory	102
6. Hydrolysis	$\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3) + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4}$ $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{OH}$	Aq solution: 50–60°C; H_2SO_4 catalyst; 4 h	75	Glycerol monochlorohydrin	Laboratory	62
7. Formals, acetals						
a. Formals	$2\text{CHCl}:\text{CH}_2 + 3\text{HCHO} \xrightarrow{\text{HCl}}$ $(\text{CHClCH}_2\text{CH}_2\text{O})_3\text{CH}_2$ $(\text{CHClCH}_2\text{CH}_2\text{O})_3\text{CH}_2 \xrightarrow[\text{H}_2\text{O}]{\text{Acid}}$ $2\text{C}(\text{HClCH}_2\text{CH}_2\text{OH}) + \text{HCO}_2\text{H}$	Ag HCl at 60°C	28	3-Chloro-1-propanol, etc.	Laboratory	117
b. Hemiacetals and mercaptals	$\text{OCl}_2\text{CHO} + \text{CH}_3\text{OH} \rightarrow \text{CCl}_2\text{CH}(\text{OH})\text{OCH}_3$		—	Chloral methyl hemiacetal, hemiacetals and mercaptals	Patent	77
8. Aldol condensation	$\text{CHCl}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CCl}_2\text{CH}(\text{OH})(\text{CH}_3)_2$	Action of KOH on a solution of chloroform and acetone		Trichloro 2,2-butanol	Commercial	1
9. Reduction						
a. Chloro aldehydes	i. $\text{CH}_2\text{ClCHCHO} + \text{HC} \rightarrow \text{CH}_2\text{ClCH}_2\text{CHO}$ ii. $\text{CH}_2\text{ClCH}_2\text{CHO} \xrightarrow{\text{NaBH}_4}$ $\text{CH}_2\text{C}(\text{H})\text{CH}_2\text{CH}_2\text{OH}$	Acrolein and HCl; used in situ Reduction by NaBH_4	75–85	1,3-Chloropropanol	Laboratory	118
b. Chloro ketones	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{Cl}$	Catalyst, Ru 5% on C; H_2O and acid; 60–90°C; 3 + h	84–100	1-Chloro-2-propanol	Laboratory	105, 111
c. Electrolytic addition	$\text{CF}_2, \text{CFCl} + \text{CH}_3\text{CCCH}_3 \xrightarrow[\text{aq}]{\text{H}_2, \text{Pt}}$ $(\text{CH}_3)_2\text{C}(\text{CH})\text{CF}_2\text{CHClF}$	Ice-cooled	95	3-Chloro-3,2,2-trifluoro-1,1-dimethyl-1-propanol	Laboratory	119
10. Nitration	$(\text{CH}_3)_2\text{CClCH}:\text{CH}_2 + \text{N}_2\text{O}_4 \rightarrow (\text{CH}_3)_2\text{C}(\text{NO}_2)\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ $[(\text{CH}_3)_2\text{CClCH}(\text{NO}_2)\text{CH}_2\text{NO}_2]$	Solvent, CCl_4 ; 2 to 3°C	—	Nitro-chloroalcohol and chloro-olefin	Laboratory	107
11. Telomerization	$\text{CH}_2\text{CH}:\text{CH}_2\text{OH} + \text{CCl}_4 \xrightarrow{\text{FeCl}_3}$ $\text{CCl}_3\text{CH}_2\text{CHClCH}_2\text{OH}$	Solvent CCl_4 ; 65–95°C		4,4,4,2-Tetrachloro-1-butanol	Commercial	80, 81

Many studies of this reaction are found in the recent literature. Perhaps their appearance in the 1960s is indicative of a lag between the industrial demand for epoxide technology and the appearance of more recent nonchlorine processes.

Hydroxyalkyl Addition

The reaction of a hydroxyalkyl group to form an alkyl ether, with removal of HCl, is a standard reaction, but it is in competition with the addition reaction of epoxides. It is a modification of the Williamson synthesis.

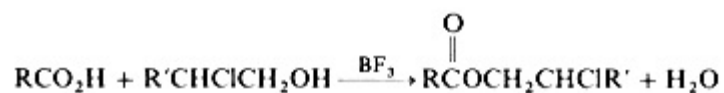
Reaction with Alcohols



Reaction with Amines. The analogous reaction takes place. Rate constants and activation energies are available for both aliphatic and aromatic amines [9].

Esterification

A chloroalkyl group may be added to an organic acid in the presence of a Lewis acid catalyst:



The esterification of chlorohydrins, and halohydrins generally, occupies a significant place in the literature.

Other Reactions

The reaction of ω -chlorohydrins, $\text{Cl}(\text{CH}_2)_n\text{OH}$, with sodium diethyl phosphite, $\text{NaOP}(\text{OC}_2\text{H}_5)_2$, is reported to give cyclic phosphonates in good yields [10].

Technology

Ethylene Chlorohydrin (2-Chloroethanol; $\text{C}_2\text{H}_5\text{ClO}$)

This product is believed to be still in actual or potential manufacture as an intermediate to ethylene oxide at one United States location only, due to special local factors, the industry generally having converted to direct oxidation processes.

However, a great deal of recent research work with this compound has

been disclosed, some of which may apply by analogy to other chlorohydrins, and some of which may be useful for smaller volume commercial outputs of ethylene chlorohydrin. A brief review is in order. For more complete discussion of large-scale processes, see the section entitled "Production from Ethylene Oxide."

Hypochlorination of Ethylene

This was a step in the major commercial route to ethylene oxide until the development of direct oxidation processes. Complete technical data were never disclosed in the literature.

A thorough laboratory study by Domask and Kobe reports conditions and yields for the conventional chlorine-water process, together with a literature survey to 1952 [11]. The data are adequate for evaluation designs and estimates. The yield of chlorohydrin on chlorine was 88.4 to 88.9% theory, with 9.1 to 9.6% ethylene dichloride formed. The data from this report were used by Myszkowski in his comparative study in 1971 [3] (Table 2, entry 1a).

The reaction of olefins with Cl^- -free HOCl is referenced in the section entitled "Propylene Chlorohydrin."

The electrochemical "chlorination" of olefins as a route to the manufacture of lower alkoxides is mentioned more fully in the section entitled "Propylene Chlorohydrin" (below).

Oxychlorination

The concern evidenced to utilize HCl as the chlorohydroxylating agent reflects the economic and environmental objective of eliminating the dilute aqueous HCl stream of the conventional hypochlorination process. Several oxidative chlorohydroxylation processes have been investigated, with reference to both ethylene and other chlorohydrins, but there are no present indications that these have been reduced to commercial practice:

TeO_2 Carrier. The claims of this patent are specific to ethylene chlorohydrin. The one example reveals a liquid-phase process in which TeO_2 , present in aqueous HCl solution, oxidizes ethylene to chlorohydrin in 89.5% yield (basis not given), precipitating metallic tellurium, which is reoxidized with O_2 in a separate operation. The ethylene chlorohydrin is removed by distillation as the water azeotrope [12] ($57 \pm 0.5\% \text{ H}_2\text{O}$, bp 97.9°C_{760}) [13].

$\text{Ti}(\text{OH})_3$ or TiCl_3 Carrier. Aqueous HCl reacts with ethylene (subsidiary examples of propylene) in the presence of thallium(III) chloride and cupric or ferric chloride, with reoxidation by O_2 . The operations can be in one, two, or multiple stage. The thrust of the patent is toward ethylene glycol, but examples show ethylene chlorohydrin in 88 to 93% yield, based on TiCl_3 converted to $\text{Ti}(\text{I})$, with lesser amounts of ethylene glycol and acetaldehyde (7 and 2%, respectively). Conditions for the separate hypochlorination with

TiCl₃ in-

clude: 0.2 molar Ti(III) in dilute aqueous HCl ; 60°C ; 73 to 78 atm; 5 h [14]. This process is misquoted elsewhere as using titanium hydroxide [16].

CuCl_2 - PdCl_2 - CaCl_2 System. This system has been studied for oxychlorination [15].

Production from Ethylene Oxide

The reverse of dehydrochlorination, namely the addition of HCl to an epoxide, may have economic potential for commercial production in cases where the foregoing processes are not suitable or economic. Laboratory studies on the preparation of the various ethylene halohydrins give rate constants for the formation of ethylene halohydrins and the secondary reaction of hydration to glycol [17]. Approaches designed to minimize this effect discuss the production of ethylene chlorohydrin in the presence of "soluble chloride" when carried out in an aqueous system, or ferric chloride and NaH_2PO_4 in the anhydrous system [1]. The potential for high yields of chlorohydrin is suggested by more recent publications. A yield of 90% is obtained in the liquid-phase reaction of ethylene oxide with gaseous HCl ; 93% is claimed for a similar reaction in anhydrous chlorohydrin as the solvent and trimethylamine as catalyst; 99% on ethylene oxide is claimed for a 200 kg-scale operation employing the same solvent at 0 to 25°C with very dilute crude ethylene oxide [18]. Elsewhere a gas-phase reaction is described in a wetted-wall reactor to facilitate heat transfer, with anhydrous ethylene chlorohydrin as the heat-transfer fluid.

The design of a manufacturing plant to carry out such suggested processes on the commercial scale requires great care from the standpoint of conditions and control because of the well-known hazard of handling ethylene oxide under circumstances where catalytic decomposition is possible. Opportunities for the occurrence of explosive conditions must be avoided by all means. Ethylene chlorohydrin is a highly toxic substance [19]. (A frequent coproduct, β , β' -dichloroethyl ether, is also identified as a carcinogen.)

Uses

Examples of the above classic reactions of ethylene chlorohydrin are:

1. Ethylene oxide manufacture: Now largely supplanted by direct oxidation of ethylene.
2. Addition of hydroxyethyl groups: Now largely carried out with ethylene oxide.
3. Esterification: A great deal of work is reported in the literature but there are no known commercial applications.

Polysulfide Rubber. The reaction of ethylene chlorohydrin with formaldehyde to produce β , β' -dichloroethyl formal [4] is used in the production of polysulfide rubber (Thiokol) [20].

Many other uses, some of which may be or may become commercial, are listed [1, 4]. The product was listed in 1975 for sale by one United States producer [19].

Physical Properties

Useful physical properties are provided by the supplier for 99 + % commercial product [19]:

Molecular weight	80.51
Specific gravity 20/20°C	1.2045
Boiling point, °C ₇₆₀	128.7
Freezing point, °C	-62.6

Properties of the water-ethylene chlorohydrin system which have been studied, include vapor-liquid equilibrium, relative volatilities, molar volumes, and molar heats of mixing [13].

Propylene Chlorohydrin (1-Chloro-2-propanol, 2-Chloro-1-propanol; C₃H₇ClO)

The large-scale industrial manufacture of propylene chlorohydrin is for its sole use as an intermediate in the production of propylene oxide. The details of its technology appear under the latter heading. The product is not offered commercially. It is suggested in the literature as an intermediate for the addition of oxypropyl groups, although in many cases propylene oxide would obviously be the reagent of choice. Other uses may be forthcoming by analogy with the chemical applications of ethylene chlorohydrin.

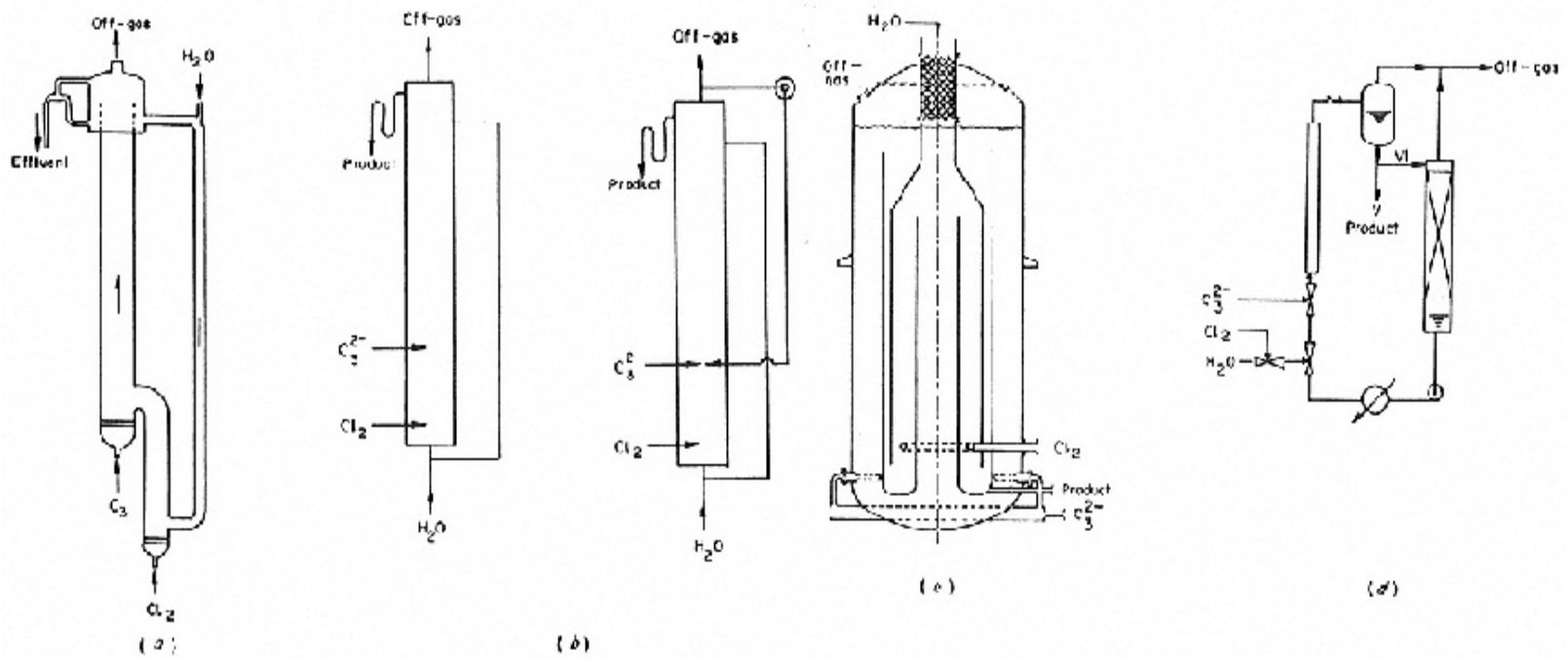
Proposed and actual processes for the manufacture of propylene chlorohydrin parallel those for ethylene chlorohydrin, with variations due to the chemical and physical differences in the reactants. Patents and other literature often include both compounds.

Methods for the production of propylene chlorohydrin in dilute aqueous solution as an intermediate are the subject of a voluminous patent literature. Methods for concentrating it, or for producing it by subordinate means such as the reaction of propylene oxide with HCl, both of which could presumably be carried out in a manner analogous to ethylene chlorohydrin, are not well described. This suggests that the pure compound has not reached important technical applications.

Hypochlorination of Propylene

This is still a major commercial process and is the subject of a recent textbook review [21] based on published information which, however, is inadequate for process design purposes [22]. As with other chlorohydrin processes which

involve contacting a slightly soluble olefin with a water solution of chlorine in which it also is only slightly soluble, equipment has been the subject of considerable ingenuity, as evidenced by the patent literature. The object is to carry out the reaction with complete utilization of chlorine while minimizing the formation of addition products of chlorine (propylene dichloride in this case) and oxidative or ether by-products. Under conventional conditions (atmospheric pressure, 40 to 50°C, 4 to 5% concentration) a yield of 90% on propylene is indicated, with 10% to by-products, mostly propylene dichloride. Figure 1 illustrates five different flow schemes out of many. The main streams are identified, and from these the principle of each can be visualized. Reference



Flow Scheme	No.	Date	To	Yield (%)			
				On Propylene		On Chlorine	
				Chlorohydrin	Dichloride	Chlorohydrin	Dichloride
a	British 738,171	October 12, 1955	Carbochimique	—	—	85-89	—
b	German 1,068,140	August 13, 1959	BASF	90-93	5.0	—	—
c	German 2,101,119	December 14, 1972	Naphthachimie	90.2?	9.1	—	—
d	British 1,359,650	December 5, 1973	BASF	99?	—	94-98	—

Fig. 1.
Five flow schemes for the hypochlorination of propylene.

must be made to the patents for details. These reactor configurations may be taken as suggestive for cases in which the olefin is volatile at the temperature and pressure of operation. In cases where the olefin is in the liquid phase, a different configuration must be used, and either dilution with an inert solvent and or intimate dispersion into the aqueous phase is specified.

A process which has implications for the hypochlorination of other olefins involves the use of HOCl in the absence of chloride ion. The reaction takes place in the presence of methyl ethyl ketone at 45°C in 30 min, giving 98% yield of propylene chlorohydrin. Also cited are 1-dodecene and 1-octadecene as olefins which can be hypochlorinated [23].

The vapor-phase reaction of propylene with chlorine in the presence of steam at 80 to 130°C with a retention time of 10 to 40 s has been studied, but no practical application is known [24].

A variant process is disclosed in German patents which follow the conventional aqueous hypochlorination of propylene by the further addition of hydrogen peroxide to the dilute chlorohydrin/HCl solution. Retention of 7 h at 75°C is reported to give 51% conversion of the HCl in 97% yield to chlorohydrin, with 47% conversion of the peroxide in 98% yield. The cost of such an operation, when optimized, would have to be balanced against savings in chlorine, lime, and waste treatment [25]. The concept is also extended to other halohydrins.

The hypochlorination of mixed olefins has been suggested, both from the standpoint of utilizing the difference in reaction rate and the greater spread in the boiling points of the epoxides, to obtain easier separations [26, 44].

The case for the electrolytic process, in which ethylene or propylene are hypochlorinated in cells in which an aqueous NaCl solution is electrolyzed, has been examined by Ibl and Selvig [27]. Yields per pass to the epoxides are 82 and 87.7%, respectively. Costs are at present considerably higher than for the existing amortized propylene oxide plants. This approach has not been extended to other olefins. (See also examples from the patent literature and various news releases [28].)

A method for the preparation of optically-active propylene chlorohydrins and oxides has been patented [29].

Butylene Chlorohydrins (C₄H₉ClO)

There are six isomers derived from linear butenes and three from isobutylene (see Table 1):

These compounds have been the subject of considerable study in recent years. Conceivably their potential use is for introducing butoxy groups into polyether-polyols to modify the properties of urethane polymers, or for other similar reactions, and for the production of butylene glycols. Whether this chemical approach, or that involving hydroperoxide chemistry, would be taken would depend on the particular circumstances prevailing. No large-scale industrial applications, except those of 1,4-butanediol, have been publicized, although several of the oxiranes and glycols are mentioned in advertising literature.

The conventional mode of hypochlorination in dilute aqueous solution was investigated by Myszkowski and Zielinski, and the results for nine olefins were reviewed by the former, as previously noted [3]. Details for six olefins, including 2-butene, are given in earlier joint publications [6, 30]. Yields of 87 and 90% theory from chlorine are reported for the corresponding vicinal chlorohydrin (CH₃CH₂ClCHOHCH₃). Likewise, 87.2% is reported for

1-butene [31]. The yield for isobutylene is not given. Table 3 shows the reported physical information and optimum conditions for the three butenes.

This work is reported at atmospheric pressure. The composition of the hydrocarbon feed is not given, so it must be assumed that yields are based on

TABLE 3 Physical Information and Optimum Conditions for Three Butenes

	1-Butene	2-Butene	Isobutylene
Solubility in water (mol/l, 20°C/760)	4.30	3.86	5.21
Dipole moment	0.37	0.00	0.49
Chlorine feed (mol/l h)	0.73	0.13	1.13
CH concentration (mol/l)	0.32	0.40	0.73
Olefin/Cl ₂ mole ratio	2.00	1.80	1.70
Temperature (°C)	45	45	50

contained olefin. The authors lay stress on water solubility of the chlorohydrin as determining its optimum concentration. Further, the output per unit reactor volume is a factor of the water solubility of the olefin and its dipole moment. Mole ratio and temperature are functions of the vapor pressures of the olefins and their chloro derivatives. By-products from 2-butene are dichlorobutane (5%), chloroether (1%), and oxidation products (2%). Conversion of the 2,3-chlorohydrin into the corresponding epoxybutane was obtained in 87% yield (12% product concentration, lime dehydrochlorination, pH 10, 100°C). By-products are glycol (11%) and ketone (2%).

A recent patent aimed at minimizing by-product formation in the hydrolysis reaction employs low temperatures and excess alkali, followed by steam stripping under reduced pressure to recover the oxirane. When 30% excess NaOH was used at 10 to 15°C or room temperature for 10 to 50 min, followed by steam stripping at 75 to 95°C overhead temperature, the yield of isobutylene oxide on chlorohydrin was 92%. With 100% excess lime at below 20 C for 20 min, the yield was 98%. Yields for 1-butylene oxide and 2-butylene oxide are not given but probably are similar [32].

When the above yield indications are combined, it appears that the overall yield of the oxirane on the olefin may be in the range of 80 to 88%, which is not radically different from that of other commercial epoxides. To this yield will be added the recoverable dichlorobutanes, which presumably would have a market value.

Table 4 gives azeotropic compositions for seven water-chlorohydrin systems [3]. (Boiling points for isomers which lack azeotropic data are given in Table 1.)

In looking toward commercial applications, both as regards butylene chlorohydrins and those of butadiene (below), not only should all of the above-referenced material be taken into account, both for theory and practice, but also the body of patent literature, particularly as regards reactor configurations that may result in designs which utilize reaction rate, solubility, and vapor-pressure characteristics of the system. For example, Fig. 1 cites British Patent 1,339,650 which substitutes for large dissolving columns a series of ejectors which attempt to make use of the high hydration rate of chlorine and its rapid reaction rate with olefin to reduce the reactor volume. High yields of chlorohydrin on chlorine are claimed (95 to 97%) [33].

TABLE 4 Boiling Points and Azeotrope Data

Chlorohydrin	Boiling Point (°C760)	Azeotrope with Water		
		Boiling Point (°C760)	CH Content	
			Wt. %	Mol %
2-Chloroethanol	128	97.8	43.5	14.85
1-Chloro-2-propanol	127	96.0	49.1	15.50
1-Chloro-2-methyl propanol-2	128	93.5	66.0	24.40
3-Chloro-2-butanol	139	94.5	58.7	19.15
1,3-Dichloropropanol-2	174	99.0	23.2	4.06
1,3-Dichloro-2-methyl-2-propanol	174	98.3	35.2	6.40

The 1,3-chlorohydrins, 3-chloro-1-butanol, and 4-chloro-2 butanol have been prepared by the reaction of aqueous HCl with butane-1,3-cyclic sulfate prepared from butane-1,3-diol [114].

Butylene Dichlorohydrins (C₄H₈Cl₂O₂)

Specific isomers of this group, prepared from acetylene or butadiene, are described in the journal and patent literature as intermediates for synthesis and for introducing halogen into urethane foams to impart fire-resistant properties.

Butynediol, produced from acetylene and formaldehyde (and other acetylenic diols), has been the subject of patents aimed at producing dichloro and tetrachloro addition compounds, and acetylenic chlorohydrins which are useful in the synthesis of bioactive products:

1. In the presence of aqueous inorganic acids, additive chlorination takes place; e.g., in 10% H₂SO₄ at 85°C the yield of CH₂OHCCl:CClCO₂H is 80.5%; the by-product is CH₂OHCCl₂CCl₂CH₂OH [34].
2. Additive chlorination at -50°C in methanolic HCl solution gave 78% of CH₂OHCCl₂CCl₂CH₂OH [35]. In the presence of light, chlorination gives the tetrachloro additive, with HO₂CCCl:CClCHO as the byproduct. The former was made predominantly at 20 to 22°C [36]. Another patent source indicates rather similar conditions for the preparation of dichloro alkanols and alkenols from alkynols [37].
3. Additive chlorination in the presence of CuCl₂ gave CH₂OHCCl:CClCH₂OH in 85 to 90% yield. After esterification to the diformate, the product was chlorinated to CH₂OHCCl₂CCl₂CH₂OH [38].

An example of the utility of these products is provided in a process for a fungicide in which the latter compound is converted to 2,2,3,3-tetrachloro-1,4-

butanediol acid phosphate by reaction with P_2O_5 in o-chlorobenzene solvent at 165°C [39].

Butynediol and pentynediol are chlorinated to replace OH groups with $COCl_2$ in the presence of catalytic amounts of N,N'-dialkyl formamides. For example, the reaction of 1,4-butyne-2,3-diol (4.99 mol) with phosgene (5.56 mol) in the presence of dimethylformamide (0.68 mol) at 50 to 60°C for 8.5 h total time gave 60.5% of theory 4-chlorobutyne-2-ol-1 and 13.8% 1,4-chlorobutyne-2. The compounds are stated to be of value as intermediates in the preparation of biologically-active products [40].

As a source of tetramethylene chlorohydrin (4-chloro-1-butanol) for further studies in the synthesis of ϵ -caprolactam, 1,4-butanediol was reacted optimally at 70 to 80°C with HCl under reflux for 5 to 7 h. The yield was 74 to 79% with 1,4-dichlorobutane and bis-chlorobutyl ether as by-products [41]. These data amplify earlier references [1].

The mixed isomers are receiving some attention, both for synthesis purposes and as a source of butadiene dioxide (2,2'-bioxirane). For the latter purpose, oxidation processes, including electrochemistry, are also proposed [28]. The mixed isomers are prepared in 60% yield from butadiene by hypochlorination with "bleaching power" (calcium hypochlorite?) in a cold (0°C) aqueous solution with addition of CO_2 [42]. The conversion of the 2,3-chloro isomer to butadiene dioxide (2,2'-bioxirane) is disclosed in a Russian patent [43].

Glycerol Chlorohydrins

Glycerol Monochlorohydrins: 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol; $C_3H_7ClO_2$.

Glycerol Dichlorohydrins: 2,3-dichloro-1-propanol, 1,3-dichloro-2-propanol; $C_3H_6Cl_2O$.

Epichlorohydrin: chloromethyloxirane; C_3H_5ClO .

The technology of these compounds is discussed in the article Glycerol, in whose manufacture they all are important intermediates. Epichlorohydrin is a commercial chemical intermediate in its own right, and although strictly not a chlorohydrin by definition, it is discussed in some detail below.

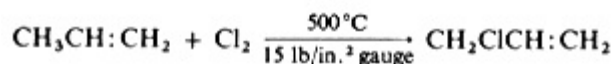
The properties of the compounds are summarized in an earlier review [1]. The methods of manufacture have not been published in detail, and such data as are available appear in brief discussions [45, 46], in reports of laboratory studies [3, 6], and in the patent literature.

Epichlorohydrin

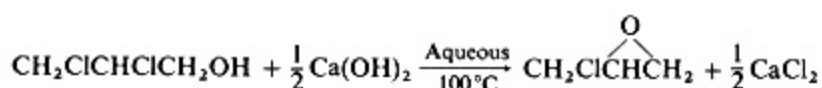
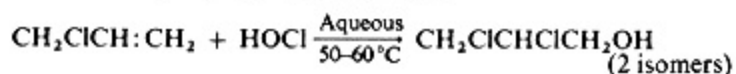
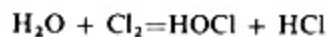
The major industrial process for epichlorohydrin still is understood to involve the high temperature chlorination of propylene to allyl chloride, followed by

hypochlorination to the dichlorohydrins, which are then dehydrochlorinated to give the oxirane. Figure 2 gives a schematic flow diagram in which the reactions shown below are carried out. The relationship of the epichlorohydrin operation to the various glycerol processes is given diagrammatically in Ref. 21, p. 242.

Vapor phase:



Dilute aqueous:



Allyl chloride is formed by the high-temperature chlorination of propylene at 650 to 950°F using a mole ratio of propylene to chlorine of 4 and a conversion of 25% of the propylene per pass. The yield of allyl chloride is 80 to 85%. By-products are hydrogen chloride and "D-D," chlorinated propane-propenes [4].

Allyl chloride is hypochlorinated with a dilute solution of chlorine in water. The temperature is maintained at 85 to 100°F. The olefin is very slightly soluble in the aqueous phase. If it is added in the vapor phase, the yield of glycerol dichlorohydrin is given as 93%; if it is dispersed as a liquid phase, a lower yield may be expected, 91% reported [6]. (This illustrates the problem of obtaining good chlorohydrin yields when working with nonvolatile olefins.) The by-product is 1,2,3-trichloropropane. The use of a nonionic surfactant to disperse the olefin has been suggested [47]. The yield increased from 88 to 94%.

The glycerol dichlorohydrins are dehydrochlorinated with an excess of lime slurry at atmospheric pressure and in the presence of live steam which is used to remove the epichlorohydrin (200 to 212°F). This is redistilled to give a specification product. Alternatively, the dichlorohydrins and/or the epichlorohydrin may be hydrolyzed to give glycerol (q.v.). The yield of epichlorohydrin in this step is 90% theory [6]. (With an asymmetric carbon atom, epichlorohydrin has two optical isomers.)

The literature data on chemical yields are often somewhat vague as to the basis on which these are calculated. The earlier references [45, 46] of 1957-1959 give the yield of allyl chloride as 80 to 85%, presumably based on chlorine, and that of glycerol as 77% on chlorine and 73% on propylene. Using the data of Ref. 6, allyl chloride yields dichlorohydrin at 92%; dichlorohydrin to epichlorohydrin, 90%; and dichlorohydrin to glycerol, 86%. (The basis is not given. However, since the difference between chlorine

yield and olefin yield lies in the greater chlorine consumption for the by-product production of a few percent of the unsaturated dichloro compound, it is not too important in these

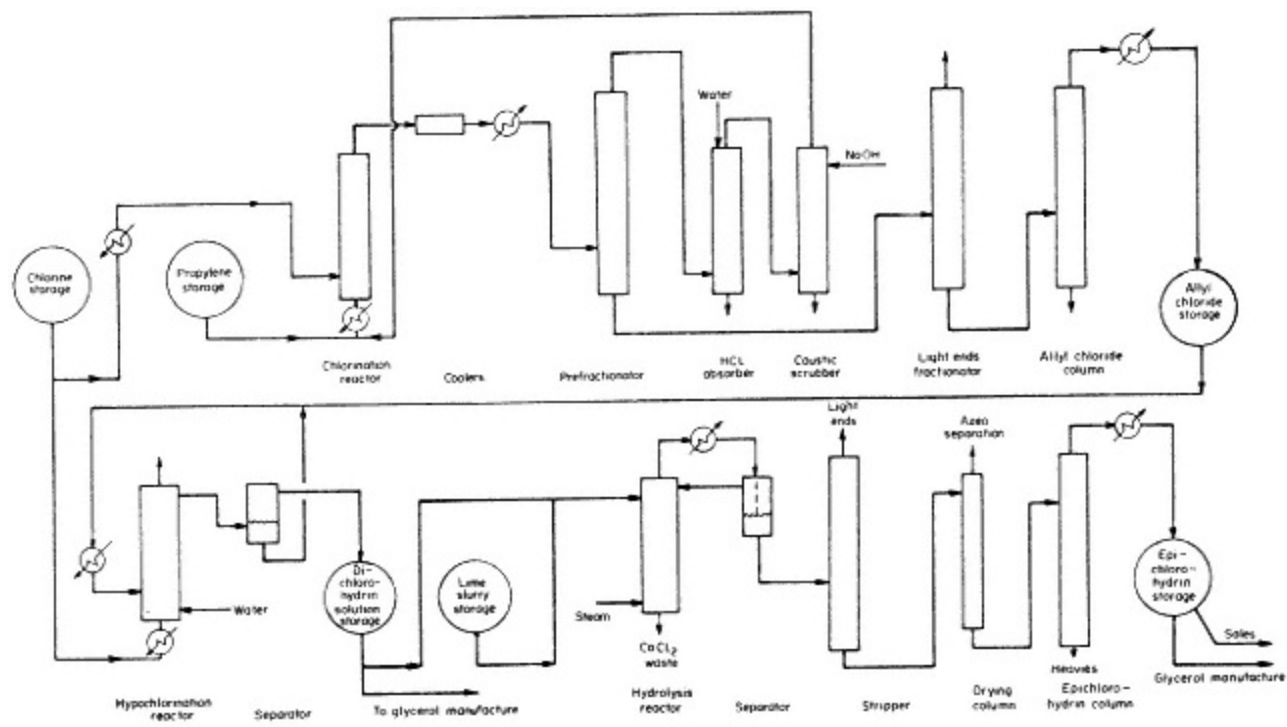


Fig. 2.
Flow sheet for epichlorohydrin production.

cases.) From these figures the yield of epichlorohydrin on chlorine or propylene may be taken as 70% theory. All of the figures permit ± 1 or 2% latitude. The difference between the recovery of glycerol and epichlorohydrin may represent a loss upon lime dehydrochlorination, which shows up as organics dissolved in the calcium chloride solution, from which they are not recoverable. A 1966 reference claims the recovery of epichlorohydrin on allyl chloride at 73% theory [48].

The above references, all dated prior to 1967, are amplified by patent disclosures on improvements since that time. The yield of dichlorohydrin on allyl chloride may be 95 to 98%. The various patents specify reactor configurations that aim at close control of conditions, introduction of allyl chloride to the chlorine-water as vapor or in a finely subdivided state, multipoint injection, and careful removal of the oil phase, trichloropropane [49]. The carrying out of the multistep hydrolysis process starting with dichlorohydrins in a plate column has been the subject of mathematical analysis [50].

There has also been a fair number of efforts reported to produce epichlorohydrin via other routes than the conventional hypochlorination. Some of the data should be mentioned, although none is known to be approaching commercial practice.

Hydroperoxide Routes. Several approaches have been disclosed:

1. Allyl chloride reacts with perpropionic acid in a countercurrent column to give 91% yield at 100% peracid conversion; mild conditions [51].
2. In a similar process peracetic acid was employed, giving 97% epichlorohydrin at 99% conversion of the peracid [52].
3. Epoxidation takes place at 51 to 54°C in 5 h employing α -phenylethyl-hydroperoxide, giving 95% selectivity on allyl chloride [53].
4. *tert*-Butylhydroperoxide epoxidizes allyl chloride in the presence of VOCl_2 and CaCl_2 as catalysts in two steps at 0 and 50°C for 1 h each to give a selectivity of 96% [54].
5. On the other hand, it is reported that epoxidation with alkyl perborates, under similar conditions which with propylene yield 79% propylene oxide, with allyl chloride yields only 38% epichlorohydrin [55]. Other peroxide compounds and catalysts also continue to be studied, indicating an actively developing technology.

Air Oxidation. The epoxidation of allyl chloride with air or oxygen is the subject of several preliminary journal reports of Eastern publication. Systems include $\text{Al-Ag}_2\text{O}$ and dimethyl phthalate-acetaldehyde. The latter is the subject of a series of publications defining conditions in a continuous system [56].

Chlorination of Allyl Alcohol. The chlorination of allyl alcohol to yield dichlorohydrins is the subject of patent disclosures. A yield of 90% is claimed in a 1966 version [57]; this is increased to 94 to 98% in a 1971 disclosure [58].

The latter carries out the reaction in the presence of HCl and a dialkyl ether. The proportion of 2,3-dichloro-1-propanol to the 1,3-chloro isomer is 87.7 to 11.9%. These techniques could be directed either toward glycerol or epichlorohydrin. Chlorination to give monochlorohydrin in 88% yield is indicated [58a].

Hydrochlorination of Glycerol. Although it is stated that chlorohydrins are no longer prepared commercially from glycerol [1], there still appear publications, particularly of Eastern origin, that tend to define this chemistry. Perhaps it should be mentioned as a "type reaction" that would be useful for synthesis under special circumstances.

The production of epichlorohydrin from glycerol via HCl hydrochlorination is illustrated by a Polish patent in which the overall yield is quoted at 79% [63]. This is comparable with the yield of epichlorohydrin from allyl chloride, 75 to 82%.

Epichlorohydrin is an important intermediate for the manufacture of polymers which find applications in surface coatings, adhesives, wet-strength resins for paper, and possibly elastomers. It is referred to in patents as a component of polyether-polyols which enhances the fire retardancy of polyurethane compositions [60]. It is also used in organic chemical syntheses.

Epichlorohydrin is toxic and has an irritating odor. Its use should be preceded by an investigation of conditions for safe handling. Good ventilation and protective clothing are requisite. Accidental skin contact areas are to be washed thoroughly.

Epichlorohydrin, in common with other epoxides, can react violently, especially under catalytic conditions, as in the presence of acids, bases, and metal salts. Contamination with other process materials is to be strictly prevented. Reactions should be carried out under closely controlled conditions with the inventory of epichlorohydrin minimized.

Specifications for the product are likely to be written around its use in polymerization reactions, and hence will be stringent. Table 5 presents the published physical properties.

The annual United States output in recent years, excluding captive use in glycerol manufacture, has been:

1967 110,000,000 lb

1968 120,000,000 lb

1972 195,000,000 lb

TABLE 5 Physical Properties of Epichlorohydrin

Molecular weight	92.5
Specific gravity (20/20°C)	1.176
Density (lb/gal)	9.8
Boiling point (°C, 595%)	115117
Freezing point, pure (°C)	-57.1

This compares with an estimated production capacity of 435 million pounds about evenly divided between Union Carbide and Dow, with Ciba listed as a smaller producer (35 million pounds). Current pricing (mid-1975) is at \$0.35 to \$0.38 in tank cars, delivered basis.

A large part of the quoted epichlorohydrin capacity appears to be devoted to the product as an intermediate for the manufacture of glycerol (q.v.). A recent review article covers the production of the latter from epichlorohydrin, including a report on optimal reaction conditions [61].

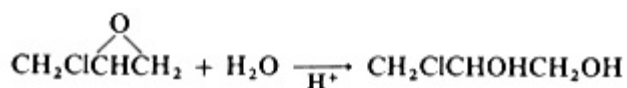
Glycerol Chlorohydrins

These compounds are produced as described above as intermediates for epichlorohydrin and glycerol. Supplementing the earlier review of properties, chemistry, and uses mentioned above, there is a continuing flow of literature which refers to applications based on their trifunctionality, such as crosslinking agents in polymers, introduction of halogen into polymers to impart fire resistance, and in various syntheses and direct biological applications. Nevertheless, there is no available information regarding actual commercial uses, availability, prices, or quantities.

Following is a review of some of the technical disclosures which have appeared in addition to the larger-scale operations described above. These might be useful for smaller-scale synthesis or as illustrative examples for analogous preparations or reactions.

Glycerol Monochlorohydrins

A batch pilot-scale preparation (60 kg) is reported in which 75% yield at 97 to 99% purity was obtained by hydrating epichlorohydrin in aqueous solution in the presence of sulfuric acid catalyst (4 h total time at 50 to 60°C initially), followed by distillation [62]:



The reaction can be carried out in the presence of bases, acids, and acid cationic exchangers.

Glycerol Dichlorohydrins

1. A procedure for reversing epichlorohydrin preparation by reacting epichlorohydrin with HCl in a thin-film reactor to produce dichlorohydrin is described. Its technical use would be unusual [63].
2. The hypochlorination of allyl chloride with NaClO, with combined

extraction of the dichlors using unreacted allyl chloride, gives the possibility of a low-energy route to pure dichlors [64].

3. The use of tert-butyl hypochlorite as a reagent for special hypochlorinations is illustrated [65]. The hypochlorite is added to a mixture of allyl chloride (217 g) and water (2500 g) with a trace of sodium formate (4 g). Contact for 4 h at 15 to 20°C gives 245 g (94%) of dichlorohydrin in solution (10%).

4. A reaction of chlorohydrins "capable of synthesizing any naturally-occurring triglyceride" has been published. The simple two-step synthesis avoids the use of blocking groups to protect the hydroxyls. The method might be used for large quantities [66].

5. An example of proposed uses of chlorohydrins in complex polymerizations is given by the reaction of 1,3-dichloro-2-propanol with epichlorohydrin to give $(\text{CH}_2\text{Cl})_2\text{COCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$. This is modified and further polymerized with propylene oxide. The allylic chlorine provides cross-linking sites (Dow) [67].

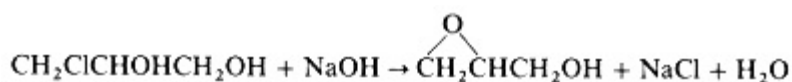
Polyhydroxy and Oxirane Compounds

The needs of modern polymer technology for compounds which will introduce multiple hydroxyl groups into molecules have suggested a variety of reactions by which various functional groups could be employed to accomplish this. The major commercial chlorohydrins, oxiranes (epoxides), and polyhydroxy compounds are discussed under the appropriate headings (q.v.).

Other polyhydroxy compounds, which may in part be derived from chlorohydrins, are far too numerous to review completely. The following are examples of some such compounds which may attain commercial status. It goes without saying that other derivations may often be competitive or preferable; for example, hydroperoxide hydroxylation or addition of oxirane groups.

Glycidol

This may be produced from glycerol monochlorohydrins by dehydrochlorination with a base such as NaOH. If the objective is to minimize glycerol formation, an organic solvent may be used, with azeotropic removal of the water formed [68]:



Glycidyl ethers may be formed by the reaction of epichlorohydrin with, for example, ethylene glycol in the presence of NaOH and an azeotroping solvent [69]. These compounds may prove useful for urethane polymers and surfactants.

Long-Chain Epoxides and Vicinal Glycols

Various methods for the formation of vicinal chlorohydrins, followed by epoxidation and/or hydrolysis to produce glycols [6], have been extended to cover long-chain olefins.

A rather detailed patent disclosure describes a procedure for making long-chain chlorohydrins which may be dehydrochlorinated to give epoxides. These are useful for surfactants [70]. In examples involving dodecene, the olefin was dissolved as a 25% solution in petroleum ether. To this was added 0.5% chloride-free aqueous hypochlorous acid in the mole ratio 1/1 at pH 6. The mixture was stirred at atmospheric pressure to emulsify the phases, and the reaction continued for 1 to 6 min at about 15°C. The phases were allowed to separate by gravity, separated, and the solvent and unreacted olefin were recovered by distillation from the chlorohydrin. Conversion was from 7 to 22% in experiments which gave the following yield distribution:

Chlorohydrins	90.92%
Dichloroalkane	1.14.2%
Other by-products	7.34.1%

A second disclosure uses acetone as a solubilizing agent to promote mutual contact of olefin and aqueous HOCl. Yields up to 80% alkyl chlorohydrins of C₁₃ to C₁₅ chain length are reported after hypochlorination for 20 min at 20°C [71]. A later disclosure suggests methyl ethyl ketone for the same purpose in the absence of chloride ion for the hypochlorination of 1-dodecene and 1-octadecene as examples of long-chain olefins which can be used [23].

Chlorination of 1-decene or oleic acid in the presence of a carboxamide/carboxylic acid azeotrope apparently bypasses the explicit chlorohydrin stage to produce vicinal long-chain glycols [72].

In another version the conventional route is modified to provide vic-chlorohydrin ethers as by the reaction of a long-chain olefin with chlorine or tert-butyl hypochlorite in the presence of ethylene glycol to yield $\text{RCHClCH}_2\text{OCH}_2\text{CH}_2\text{OH}$, R=10 to 14 C. The hydroxyl group is sulfated and the sodium salt is formed. The product is a superior surfactant [73].

It will be noted that several patents involving hypochlorination and epoxidation suggest long-chain olefins as subsidiary examples. There may be technical reasons for giving analogies over a wide spread of molecular weight, or experimental convenience may be involved, but they do suggest extensions of the technology. Commercial applications have not been publicized.

Other Polyhydroxy Compounds

Conventional methods may be employed for these. The synthesis of 1-chloro-2-methyl-2,3-propanediol by the hydroxylation of methallyl chloride using 30% H₂O₂ in formic acid is reported, but no yields are available [74]. The method of hypochlorination of methallyl alcohol and its hydroxylation to 2-methyl-1,2,3-propanetriol are described as research interests [75]. A

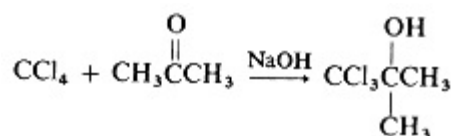
number of chloroether glycols have been prepared and characterized; for example, $\text{CH}_2\text{ClCH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_4\text{OH}$ by the reaction of epichlorohydrin with glycols in the presence of BF_3 etherate [76].

Polychloro Halohydrins and Oxiranes

A rather wide range of activity has been apparent in compounds of this nature. At least a part of the interest has had to do with products which reduce the flammability of polymers. In such uses the polyfunctionality of the chlorohydrin molecule leads to polymer chain extension while the remaining chloro groups have the desired effect on flammability. Other applications of these compounds are also in evidence. A common method of introducing the polychloro moiety is by the reaction of carbon tetrachloride or chloroform with olefins or alcohols, respectively.

1,1,1-Trichloro-2-methyl-2-propanol

This is formed by the aldol condensation of acetone and chloroform:



and is known variously as "chlorobutanol," "acetone chloroform," and "Chloretone." This chlorohydrin is an old commercial product with medicinal uses (Encyclopedia of Chemical Technology, Vol. 5, 2nd ed., Wiley, New York, 1964, p.122).

A somewhat similar group of 25 compounds, chloral hemiacetals or hemimercaptals, $\text{CCl}_3\text{CH}(\text{OH})\text{XR}$ ($\text{X} = \text{O}$ or S), were prepared by conventional methods in a study of herbicidal activity. Some are claimed to be effective [77].

1,3,3,3-Tetrachloro-2-methyl-2-propanol

This and other tetrachloro and pentachloro isomers are formed by the lightactivated direct chlorination of 1,1,1-trichloro-2-methyl-2-propanol in carbon tetrachloride solution at 65°C [78]. The tetrachloro compound is dehydrochlorinated to give the oxirane, 2-trichloromethyl propylene oxide, by treatment with caustic soda in 96% yield of 97% pure product. The product is a contact insecticide [79].

2,4,4,4-Tetrachloro-1-butanol

Synthesis by the telomeric reaction of carbon tetrachloride and allyl alcohol takes place in the presence of an excess of CCl_4 (3/1 mole ratio) and a catalyst system

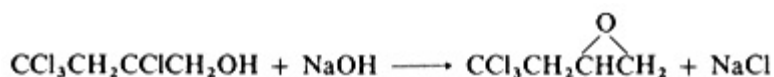
consisting of iron powder, with or without FeCl_3 , or with FeCl_3 , CaCO_3 , and MgSO_4 [80, 81]. The chlorobutanol may be dehydrochlorinated with caustic or lime to produce the epoxide [82], or it may be used unchanged to esterify organic acids [83].

The commercialization of the halogenated epoxide 4,4,4-chloro-1,2-epoxybutane has been announced [84]. The process may be reasonably visualized from the patents quoted. Following the more recent reference [81]: carbon tetrachloride and allyl alcohol are mixed in the molar ratio of CCl_4 /alcohol 24 to 1 in a reactor suitable to resist chloride corrosion (glass, etc.). Iron powder and FeCl_3 are added, and the charge is heated under reflux 5 to 8 h at 65 to 95°C. Side products of the reaction are water and HCl. Following the reaction the catalyst is removed by filtration, the excess CCl_4 recovered, and the product may be purified by distillation or it may be used crude in the subsequent step. The yield of chloroalcohol is 70.5% based on 96% conversion of allyl alcohol; yield on CCl_4 consumed is 86% theory.



The crude chlorobutanol may be dehydrochlorinated in the conventional manner, using lime slurry, to produce 4,4,4-trichloro-1,2-epoxybutane, which may be recovered by distillation. However, a later reference [82] emphasizes the technical and economic advantages of using the crude dehydrochlorinated mixture for subsequent polyol manufacture.

Following this procedure, the crude chlorobutanol containing CCl_4 as a solvent is reacted with dilute (4%) NaOH solution which is introduced slowly, avoiding an excess, at 60°C. The reaction takes place over 2 1/2 h, after which the phases are separated and the aqueous NaCl solution is washed with CCl_4 . The organic layers are combined and stripped of CCl_4 , leaving the crude product which is 73% 4,4,4-trichloro-1,2-epoxybutane plus unconverted chlorobutanol and other organics. The yield is 82% epoxybutane based on the tetrachlorobutanol charged.



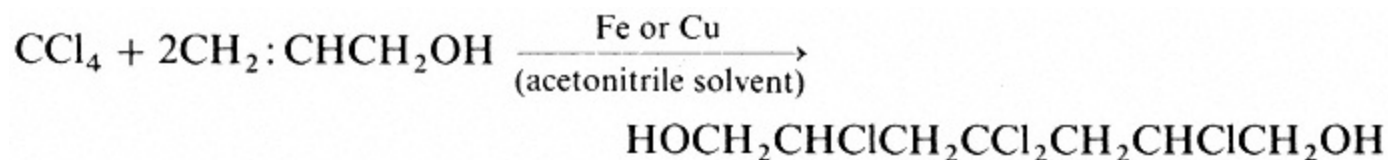
Certain features of the process will occur to the technologist: (1) that conditions where acid aqueous HCl can appear require corrosion-resistant equipment; (2) that the route which avoids product distillation will maximize yield and decrease energy requirements; (3) that any such process which involves epoxides, particularly under conditions where the oxirane ring may open (acidic, basic, etc.), should be treated carefully from the standpoint of safety; and (4) that the process should be amenable to continuous operation.

A somewhat different technique employing iron carbonyl catalyst and butanol/ CCl_4 solvent is claimed to yield 88% of the tetrachlorobutanol on the allyl alcohol consumed [85].

The product may also be made from allyl acetate (which occurs as an intermediate in one allyl alcohol process) by telomerization with CCl_4 in the

presence of benzoyl peroxide, followed by hydrolysis of the ester. The latter step, given as a laboratory procedure employing methanol and chloroacetic acid, gave 97% yield on the tetrachlorobutyl acetate as tetrachlorobutanol. This was oxidized by chromic oxide in acetic acid/water to give tetrachlorobutyric acid in 51% yield [86].

Recent studies which showed that not only telomerization but also twofold addition would take place are perhaps of more theoretical interest. They do point a way to the formation of chloro-diols, for example, 2,4,4,6-tetrachloroheptane-1,7-diol [87]:



2-Chloromethyl Epichlorohydrin

Another method to introduce an oxirane group to a polyhalogenated olefin is by epoxidation with a peracid:



In an example, 3-chloro-2-chloromethyl-1-propene is epoxidized with performic acid which is formed from 70% hydrogen peroxide and formic acid. The olefin is added at 25 to 27°C over 20 min, the mixture is held 2 h at that temperature, and then at 50°C for 2 h. The product is recovered by extraction and distillation of the unreacted olefin (conversion, 68%). The yield is 76% theory on olefin converted. This olefin is a by-product of the manufacture of methallyl chloride [88].

Trichloropropylene Oxide (C₃H₃Cl₃O; 3,3,3-trichloromethyl Oxirane)

This compound is not otherwise described than in a patent in which it is employed in the preparation of a complex polyether polyol [89] and as an oxirane which may be copolymerized with vinyl compounds. Presumably it would be synthesized by dehydrochlorination of 1,3,3,3-tetrachloro-2-propanol [79].

Other Polyhalogenated Alcohols

Several approaches to the introduction of chlorine into alcohols are described. Some of these are illustrative of methods, although not all have commercial applications.

1. The telomerization reaction described above has been induced by γ -

radiation [90]. Irradiation and heating a mixture of ethanol and perchloroethylene at 120°C for 17 h gave 35% of tetrachloro-1-butanol and trichloro-3-buten-1-ol [91].

2. Production of polyhalohydrins by direct oxidation of chlorine-containing olefins with oxygen in the presence of a catalyst (cobalt salt, etc.), a promoter (Mg, etc.), and an activator (peroxides) is claimed. Presumably the oxidation of the raw material provides the source of the added chlorine, and yields appear to be low (28% in one example) [92].

3. Conditions for the dehydrochlorination of β -methylglycerol dichlorohydrin to 2-methyl-epichlorohydrin are given by Myszkowski [3]. Further details of the reaction, and of the subsequent hydrolysis to β -methylglycerol, are given elsewhere [93]. Yields are not stated. The optimum conditions for the dehydrochlorination by lime are ~ 50 min at 25 to 30°C.

4. The application of the Prins reaction to the preparation of polychlorinated alcohols from chloro-olefins and formaldehyde via the formal, followed by hydrolysis, has been studied and may be quoted as an example of a method having broader potentials [117].

Complex Compounds

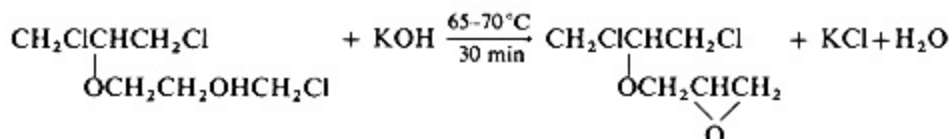
More complex products are discussed in the recent literature, and some of these may be expected to assume commercial importance as the technology of polymeric systems matures. Since the products, their manufacture, and their end uses are almost entirely proprietary, not many of them can be identified as being in actual technical use.

An example of a chlorohydrin structure which involves several typical reactions in its preparation is given in a disclosure of the synthesis of 1-chloromethylvinyl-1-glycidyl ether as one of a group of copolymerization agents for the vulcanization of rubber [94, 95];

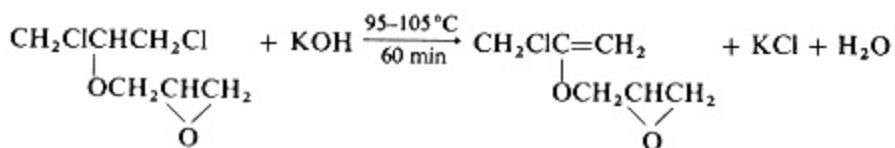
Step I: Glycerol dichlorohydrin and epichlorohydrin react in the presence of BF₃-etherate catalyst:



Step II: The chlorohydrin ether is dehydrochlorinated under mild conditions to yield the oxirane:



Step III: The oxirane is further dehydrochlorinated under more severe conditions to yield the vinyl compound:



The overall yield on dichlorohydrin and epichlorohydrin is 57% theory.

Chlorofluoro Alcohols

In an exceptional case, the hydroxyl group may be supplied by the reduction of a carbonyl group. The following compounds are prepared from halogenated acetone by reduction with NaBH₄ in diglyme solution:

1,1,1,3,3-pentachloro-3-fluoro-2-propanol

1,1,1,3,3,3-hexachloro-2-propanol

1,1,3,3-tetrachloro-1,3-difluoro-2-propanol

Direct photochemical chlorination or SbF₅ catalyst also gave good yields. These compounds are variously nematocides and antifertility agents for houseflies. Technically, they are halohydrins [96].

The electrochemical fluorination of glycerol 1,3-dichlorohydrin has been studied [97].

Complex, highly fluorinated carbinols, ketones, and polymers, some of which may contain chlorine, are beyond the scope of this review [98].

Miscellaneous Chlorohydrins (Table 6)

A few compounds of this category, which do not fit the above grouping and which either have technical significance or are illustrative of types which might become commercial, are illustrated below. Again, it is not possible to include all compounds which have been studied because of their large number.

Trimethylene and Tetramethylene Chlorohydrins

These compounds are not listed as being commercially available in the United States [99]. Their chemistry has been described elsewhere [1]. Continued research interest is indicated by a recent patent which describes the preparation of the latter from butyl hypochlorite in 49% yield and conversion to tetrahydrofuran by boiling with NaOH [100]. Trimethylene chlorohydrin has been prepared by the addition of HCl to the double bond of acrolein, followed by reduction of the aldehyde with NaBH₄; yield is 75 to 85% [118]. Kinetics for the hydrolysis reaction of trimethylene chlorohydrins have been reported [101].

TABLE 6 Miscellaneous Chlorohydrins: Homologous Groups from Recent Literature and Patent Sources

Compound Group	Structure	Formula	Boiling Point (°C, mm)	Other Data
Polychloro alcohols, unsaturated	CCl ₂ : CHCH ₂ OH	C ₃ H ₄ Cl ₂ O	888916	
	CCl ₂ : CCICH ₂ OH	C ₃ H ₃ Cl ₃ O	81.515	
			74753	
	CH ₂ OHCCI: CCICH ₂ OH	C ₄ H ₆ Cl ₂ O ₂		mp 78
	CCl ₂ : CCIC(CH ₃)(OH)CH ₃	C ₅ H ₇ Cl ₃ O		
	CCl ₂ : CCICHOHCH ₂ CH ₃	C ₅ H ₇ Cl ₃ O		
	CCl ₂ : CCIC(CH ₃) ₂ (OH)	C ₅ H ₇ Cl ₃ O	8586.515	
	CCl ₂ : CCICH(C ₂ H ₅)(OH)	C ₅ H ₇ Cl ₃ O	9011515	
	CCl ₂ : CCICH(C ₃ H ₇)(OH)	C ₆ H ₉ Cl ₃ O	9315	
Polychloro alcohols, saturated	CHCl ₂ CH ₂ CH ₂ OH	C ₃ H ₆ Cl ₂ O	178.5	d ₂₅ 1.316
	CCl ₃ CH ₂ CH ₂ OH	C ₃ H ₅ Cl ₃ O		
	CHCl ₂ CCl ₂ CH ₂ OH	C ₃ H ₄ Cl ₄ O	979915	d ₂₀ 1.15977
			86886	
	CCl ₃ CHClCH ₂ OH	C ₃ H ₄ Cl ₄ O	210	d ₁₆ 1.678
			83846	mp 3738
	CH ₃ CHClCHClCH ₂ OH	C ₄ H ₈ Cl ₂ O	9810222	
	CH ₂ ClC(CH ₃)(OH)CH ₂ Cl	C ₄ H ₈ Cl ₂ O	62.814	d ₂₀ 1.407
	CH ₂ OHCHClCHClCH ₂ OH	C ₄ H ₈ Cl ₂ O	1401441	
	CH ₂ ClCHClCH(OH)CH ₂ Cl	C ₄ H ₇ Cl ₃ O		
	CCl ₃ C(CH ₃)(OH)CH ₃	C ₄ H ₇ Cl ₃ O	166	
	CHCl ₂ CCl ₂ CHOHCH ₃	C ₄ H ₆ Cl ₄ O	9910114	
	CH ₂ OHCCl ₂ CCl ₂ CH ₂ OH	C ₄ H ₆ Cl ₄ O ₂	175185	mp 259
	CHCl ₂ CCl ₂ CH(CH ₃)(OH)	C ₄ H ₆ Cl ₄ O	10615	
	CHCl ₂ CCl ₂ CH(C ₂ H ₅)(OH)	C ₅ H ₈ Cl ₄ O	11315	
	CHCl ₂ CCl ₂ CH(C ₃ H ₇)(OH)	C ₇ H ₁₀ Cl ₄ O	12315	
	CCl ₃ C(CH ₃)(OH)CHCl ₂	C ₄ H ₅ Cl ₅ O	11211	
	CCl ₃ C(CH ₂ Cl)(OH)CH ₂ Cl	C ₄ H ₅ Cl ₅ O	11911	


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Compound Group	Structure	Formula	Boiling Point (°C, mm)	Other Data
	<chem>CCBC(CH2Cl)(OH)CHCl2</chem>	<chem>C4H4Cl6O</chem>		
	<chem>CCBC(CH3)(OH)CH2CH3</chem>	<chem>C5H9Cl3O</chem>	8716	
	<chem>CHCl2CH2C(CH3)ClCH2OH</chem>	<chem>C5H9Cl3O</chem>	7883.3.4	
	<chem>CCBC(CH3)(OH)CHClCH3</chem>	<chem>C5H8Cl4O</chem>	11812011	
	<chem>CH2OHCCl2CCl2CH2CH2OH</chem>	<chem>C5H8Cl4O2</chem>		mp 114
	<chem>CHCl2CCl2CHOHCH2CH3</chem>	<chem>C5H8Cl4O</chem>		
	<chem>CHCl2CCl2C(CH3)(OH)CH3</chem>	<chem>C5H8Cl4O</chem>		
	<chem>CCBCCl2CH2CHClCH2OH</chem>	<chem>C5H6Cl6O</chem>	11511819	
	<chem>(CH3CHCl)2CHCH2OH</chem>	<chem>C6H12Cl2O</chem>	7375151	d20 1.1800
	<chem>CH3(CH2)7CHClCHCl(CH2)7CH2OH</chem>	<chem>C18H36Cl2O</chem>		
	<chem>CH2ClCHCl(CH2)4OH</chem>	<chem>C6H12Cl2O</chem>	90911	d20 1.1805
Chloro epoxides			405050	
			455030	
				d20/15 1.3112
			432	
			707110	
			525410	
			606310	d 1.3207
Chloroether glycols	<chem>CH2ClCHOHCH2OC2H4OH</chem>		1161192.5	d20 1.4680
	<chem>CH2ClCHOHCH2O(CH2)4OH</chem>		1511522.5	d20 1.1700
	<chem>(CH2ClCHOHCH2OC2H4)2</chem>		1931952.5	d20 1.2274
	<chem>CH2ClCHOHCH2O(CH2)5OH</chem>		1581602.5	d20 1.1375
	<chem>CH2ClCHOHCH2OC2H4OH</chem>			
	<chem>CH2ClCHOHCH2O(CH2)4OH</chem>			
	<chem>(CH2ClCHOHCH2OC2H4)2</chem>			
	<chem>CH2ClCHOHCH2O(CH2)5OH</chem>		1641652	
	<chem>C10H21CHClCHOC2H4OH</chem>			

(continued)

TABLE 6 (continued)

Compound Group	Structure	Formula	Boiling Point (°C, mm)	Other Data
Trimethylene chlorohydrins ^a	CH ₃ CH(OH)CH ₂ CH ₂ Cl		676820	d ₂₀ 1.069
	C ₂ H ₅ CH(OH)CH ₂ CH ₂ Cl		757615	d ₂₀ 1.049
	n-C ₃ H ₇ CH(OH)CH ₂ CH ₂ Cl		818210	d ₂₀ 1.019
	i-C ₃ H ₇ CH(OH)CH ₂ CH ₂ Cl		727310	d ₂₀ 1.029
	n-C ₄ H ₉ CH(OH)CH ₂ CH ₂ Cl		1001023	d ₂₀ 0.999
	t-C ₄ H ₉ CH(OH)CH ₂ CH ₂ Cl		90923	d ₂₀ 1.009
	Cyclo-C ₆ H ₁₁ CH(OH)CH ₂ CH ₂ Cl		13814010	d ₂₀ 1.079
	Phenyl-CH(OH)CH ₂ CH ₂ Cl		1251266	d ₂₀ 1.159
	Phenyl-CH ₂ CH(OH)CH ₂ CH ₂ Cl		1401422	d ₂₀ 1.139
Pyran, 2-chlorotetrahydro			545520	
Chlorofluoro alcohols	The following analogous series are reported, but without physical data [96]:			
	CCl ₃ CH(CCl ₂ F)(OH) (bp 6945)			
	CCl ₃ CH(CCl ₃)(OH)			
	CCl ₂ FCH(CCl ₂ F)(OH)			
	CCl ₃ C(CF ₃) ₂ (OH)			
	CH ₂ ClC(CF ₃) ₂ (OH)			
	CHCl ₂ C(CF ₃) ₂ (OH)			
	CCl ₃ C(CF ₂ Cl) ₂ (OH)			
	CClF ₂ C(CF ₂ Cl) ₂ (OH)			

^aData on the analogous series of epoxides also are given.

The laboratory preparation of a series of substituted trimethylene chlorohydrins and of the epoxides derived from these, and also from 2-chlorotetrahydropyran (18 compounds), provides physical identification and some yield data for the two series [105].

Hydroxyethyl Chlorohydrins

The reaction products of ethylene oxide and ethylene chlorohydrin ("diglycol-, triglycol-chlorohydrin," etc.) have had some commercial interest but are not currently advertised. Their preparation has been investigated in the presence of acids and bases as catalysts, and procedures for higher and lower molecular weight products have been defined [102]. The reaction rates and activation energies have been determined for the addition reaction with various amines [103].

Isoprene reacted with HOCl to give 1-chloro-2-methyl-3-buten-2-ol, which was further used in organic syntheses, and 1,3-dichloro-2-methyl-2,4-butanediol [104].

Hypochlorination of an olefin with tert-butyl hypochlorite, while too expensive a technique for large volume, low-cost products, offers a high-yield route to specialties. The use of this reagent has been mentioned in the section entitled "Glycerol Dichlorohydrins" [65].

Chloroether Alcohols

These were produced by reaction between propylene oxide and chlorine, moderated by the presence of phenol. A complex mixture formed which included chloroalcohols of the type $\text{Cl}(\text{C}_3\text{H}_6\text{O})(\text{C}_3\text{H}_6\text{O})_x\text{H}$ ($x = 1, 2, \text{etc.}$) along with chlorophenols [106].

Nitro Chlorohydrins

The reaction of N_2O_4 with chloro-olefins at -2 to 0°C gives chlorohydrins which contain a NO_2 group: an example is $(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ [107].

Styrene Chlorohydrin

Earlier studies of the hypochlorination of styrene in which high yields were reported are corrected by work in which "substantial quantities" were produced and in which it was found that the presence of β -chlorostyrene accounts for part of the earlier yield, calculated as styrene oxide. In the new work the yield was improved by increasing the mutual solubility of styrene and water by adding acetone to the system [108].

In a typical experiment, 1.25 mol of styrene in 1000 ml acetone and 250 ml

water, with 0.5 mol sodium carbonate, were treated with 1 mol of gaseous chlorine at room temperature (rising to 41°C). Yields were:

Styrene chlorohydrin	72%
β-Chlorostyrene	7%
Styrene dichloride	13%

Which isomer was produced is not stated.

The work was extended to include hypochlorination of cyclohexene and 1-pentene. Theoretical studies on rate constants, etc. are reported in the Russian literature [109].

Pentaerithritol chlorohydrins receive some mention. The basis of a process for the dichlorohydrin is provided by a disclosure that pentaerithritol may be dissolved in already formed dichlorohydrin, treated with HCl over 8 h at 160 to 170°C, and distilled to yield 83% dichlorohydrin [110]. Presumably, the process can be modified to give mono- or trichlorohydrin predominantly, if desired.

Halo acetals and ketones, formed by the reaction of chlorohydrins with glycols, may be reduced by hydrogenation by using 5% Ru on carbon in the presence of water and p-toluenesulfonic acid (catalyst for the acetal reaction) [111]. Conditions are 60 to 90°C, 3 to 20 h, and 4 to 10% catalyst for various preparations. Yields of 84 to 100% of monohalogenated alcohols were obtained.

Alkoxetanes

The chlorination of allyl alcohol in the presence of an excess of various alcohols leads to the formation of alkoxychloropropanols in yields of 65 to 80% for the three main products [112]:



The conditions were moderate, C₁ to C₁₂ alcohols were studied, and the general chemistry of chlorohydrin and alkoxychloropropanol formation were reviewed.

Conversion of the alkoxychloropropanols to alkoxetanes is reported in yields of 55 to 75%:



Aqueous NaOH at 100 to 110°C was added to the alkoxy compounds and the reaction carried out over 2 to 10 h. Commercial applications of the products are not discussed.

The kinetics of the alkaline reaction to produce oxetanes from 1,3-

bifunctional compounds such as $\text{RCHOHCH}_2\text{CH}_2\text{Cl}$ have been published [113].

General

The above review has been written from the standpoint of the technologist who may wish a general update in the varied field of chlorohydrin techniques which may verge on commercial practice. It is not a review of uses, which too often are obscure.

In the preparation of any specific chlorohydrin by hypochlorination, especially in cases where the olefin is not volatile or notably soluble, the various techniques described above to ensure rapid contact of the olefin with the chlorine solution should be noted for possible yield improvement. Examples are solubilizing by a mutual solvent, dispersion by high-energy mixing or by the use of a surfactant, and effective separation of the insoluble by-product phase. The various proposals to reduce the formation of chlorine addition products by the use of HOCl free of chloride ion are of interest. The discussions by Myskowski represent a major contribution to an understanding of hypochlorination and hydrolysis reactions. Very little other material which can be used as an engineering basis for chlorohydrin technology has appeared.

Physical and Process Data

The paucity of published data which would be applicable to the technology of the chlorohydrins is not surprising considering the proprietary nature of much of the information and the fact that most of it appears in patent literature of the past two decades.

Ethylene chlorohydrin and epichlorohydrin are well-characterized as chemical intermediates (see above, and Refs. 1, 2, and 19). The azeotropic system water/ethylene chlorohydrin has been studied at 100 mmHg, and vapor-liquid equilibrium data have been published [13]. The effect of pressure and liquid composition has been studied [119a]. The extraction of ethylene chlorohydrin in several ternary systems was studied [120]. The vapor-liquid equilibria of ethylene oxide with impurities in the chlorohydrin process, including the latter compound, have been reported [121].

The items in Table 7 are given by Myszkowski [3] for a group of 10 olefins and their corresponding chlorohydrins and dichloro derivatives (not all items for each group).

The surface tension for 10 different chlorohydrins as a function of concentration and temperature has been published [122].

Partition coefficients involved in the extraction of glycerol dichlorohydrins from dilute aqueous solutions, given in a series of patents assigned to Pittsburgh Plate Glass, are more properly a subject to appear in the Glycerol article.

TABLE 7 Process Data for 10 Chlorohydrins

	Olefins	Chlorohydrins	Dichloro Derivative
Water solubility	×	×	
Vapor pressure	×		×
Azeotropic data		×	
Dipole moment	×		

Good process corrosion data are essentially lacking. One study of the thermal stability of ethylene chlorohydrin and its corrosiveness is given partly in terms of alloys having Russian designations [123].

Most of the physical properties reported in the patent literature are given for compound identification, and as such may have varying degrees of precision. The boiling points at a given pressure, presented in Tables 1 and 6, are the most useful single datum for technical considerations. Density and melting point are sometimes available. In some cases, index of refraction, etc, also appear in the referenced material. Some additional data are to be found in the earlier review [1].

Many of the chlorohydrins contain asymmetric carbon atoms, and as such have optical isomers. These are hardly mentioned in the technical literature, except in one case (propylene chlorohydrin), and are not discussed above.

Toxicity, Pathology, Safety

The warnings which are given above and in the earlier review [1] concerning the hazards of some of the simpler chlorohydrins may be expanded into a general recommendation that all compounds of the nature of chlorohydrins should be circumspectly handled until their physiological impact is known. The production of most of them is associated with other materials (chlorine, HCl, olefins, etc.) which have well-known toxic, irritant, or flammable properties.

Both the industrial and legislative viewpoints with respect to such classes of compounds as chlorohydrins are in a state of review and change. At this point it is considered adequate to indicate some of the major sources which may be consulted with respect to specific compounds.

The Employment Safety and Health Guide [124] contains the provisions of the Occupational Safety and Health Act (OSHA), as taken from the Federal Register, and should be consulted for those compounds which are actually specified as toxic, some of which are regulated. Information on specific compounds may be obtained from the National Institute of Occupational Safety and Health (NIOSH) [125] via a computerized data bank. The Toxic

Substances List, compiled by NIOSH, also should be consulted [126]. Other listings of range-finding and subacute inhalation toxicity data appear in the journal literature [128]. Few case studies of specific chlorohydrins are found in the chemical literature [129].

Generally, good safety practices for laboratory, pilot plant, and industrial operations are recommended, with due regard for such factors as the possible permeability of gloves and other protective equipment by the materials handled, and strict limitations on inhalation or ingestion. Where applicable, certified personal safety equipment may be specified [127].

Environmental

The most commercially-significant processes by which chlorohydrins are made and converted into epoxides have internal and/or waste streams that are dilute aqueous solutions of HCl or alkali metal chlorides, and which have in them minor amounts of organic chloro, hydroxylated, and ether by-products. These present considerable problems for their disposal into the environment. New products of a similar nature may also present difficulties in waste disposal. The employment of dilute solutions in processing results in the discharge of considerable volumes of wastewater.

The amount of contaminants which reach the environment may be reduced in various ways: (1) by increasing the concentration of the chlorohydrin; (2) by recovery of the contaminants, (by evaporation, by adsorption, or by recycling, as to electrolytic cells); and (3) by biological oxidation.

The first two methods can be evaluated by engineering studies and are the subject of a voluminous patent literature. The third method removes organic contaminants but not soluble chlorides. Each of the methods is subject to definite economic limitations. Generally, there is no method to economically recover water-soluble chlorides or organics.

Methods for biological oxidation of the organics in chloride-bearing solutions have been under study for some years. Most of the practical information is proprietary, hence it is not feasible to indicate design parameters or economic factors for this operation. In fact, the particular composition of each waste to be treated has such an effect upon the rate of oxidation that the meeting of any set criterion for discharge of the effluent is a matter for explicit experimental determination.

In commercial practice the chlorohydrin wastes end up as effluents from epoxide processes, and would be treated under those headings. One treatment study (ethylene and propylene oxide) is referenced here as an example of the bio-oxidation approach [130]. The relative biodegradability of four chlorohydrins and of other related compounds is the subject of a laboratory study [131].

Other requirements for protection of the environment, including gaseous, liquid, or solid

streams, are generally a matter of good engineering to contain the materials and avoid contamination.

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Chloromethanes

E. M. DeForest

Introduction

When hydrogen atoms of the methane molecule are substituted with chlorine, a family of chemical compounds results commonly known as the chloromethanes. Part or all of the hydrogen atoms can be substituted. If one hydrogen is replaced, methyl chloride (CH_3Cl) is the resulting compound; two hydrogen substitutions, methylene chloride (CH_2Cl_2); three, chloroform (CHCl_3); and if all four hydrogens are substituted, carbon tetrachloride

(CCl_4) is the resulting compound. All of these chemicals have a family resemblance but are distinct individual products with their own differing properties.

The existence of chloromethane compounds has been known for many years; probably chloroform was the first chloromethane to be produced in the laboratory. History indicates that three independent investigators almost simultaneously isolated chloroform. Samuel Guthrie in the United States, J. von Liebig in Germany, and E. Soubeiran in France announced the discovery of the chloroform molecule in 1831. In 1835, Dumas and Peligot heated methanol with sulfuric acid and sodium chloride to produce methyl chloride. Regnault is credited with the first isolation of carbon tetrachloride in 1839 by chlorinating chloroform. In 1840 he produced methylene chloride by similarly chlorinating methyl chloride.

The first commercial use of any of the chloromethanes was probably that of chloroform when Sir James Simpson of Scotland first used it as an anesthetic in 1847 [1]. It was used extensively for surgery for nearly 20 years, virtually displacing ether, but after a long record of accidents from its use, it lost favor with surgeons and they again turned to the use of ether. With the advent of the chemical age, uses for all four of the chloromethanes have been discovered. Today they are used extensively in industry, and new uses continue to be developed. Approximately 1.1 million tons of chloromethanes were produced and consumed in the United States in 1975.

Production

There are 11 manufacturers of chloromethanes in the United States. Some produce only methyl chloride for captive use. A list of these producers showing the location of their manufacturing facilities is shown in Table 1. The total production of chloromethanes in the United States for the past 10 years is given in Table 2.

Applications

Methyl Chloride

One of methyl chloride's first uses was as a refrigerant in small refrigeration units. It is still used to some extent for this purpose. A significant application is that as a catalyst carrier for polymerization reactions such as butyl rubber. It is also used for the preparation of silicones by direct reaction with silicon metal; as an aerosol propellant where it is combined with methylene chloride, propane, and Freon-12 for various aerosol mixes; and as a methylating agent in certain organic syntheses. Some manufacturers of foam plastics use it as a blowing agent. Its solvency properties and low boiling point make it a good extractant for heat sensitive compounds. Methyl chloride poses some hazards from chemical reactions with other compounds. It will form spontaneously flammable trimethyl alumina when mixed with powdered metallic aluminum. An explosion can result from contact with magnesium, and it reacts explosively with metallic sodium or other alkali metals.

TABLE 1 Producers of Chloromethanes in the United States

Company	Location	Products Manufactured			
		CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
Allied Chemical Corp. (Solvay Process Division)	Moundsville, West Virginia	×	×	×	×
Ancon Chemical Co.	Lake Charles, Louisiana	×			
Ansul Chemical Co.	Marinette, Wisconsin	×			
Diamond Alkali Co.	Belle, West Virginia	×	×	×	
	Painesville, Ohio				×
Dow Chemical Co.	Freeport, Texas	×	×	×	×
	Plaquemine, Louisiana				×
Dow Corning Corp.	Midland, Michigan	×			
E. I. du Pont de Nemours & Co. (Electrochemical Dept.)	Corpus Christi, Texas			×	×
Ethyl Corp.	Baton Rouge, Louisiana	×			
FMC Corp. (Westvaco Chlor-Alkali Division)	S. Charleston, West Virginia				×
General Electric Co. (Silicone Products Dept.)	Waterford, New York	×			
Pittsburgh Plate Glass Co. (Chemical Division)	Barberton, Ohio				×
Stauffer Chemical Co.	Louisville, Kentucky		×	×	×
	Niagara Falls, New York				×
Vulcan Materials Co. (Chemicals Division)	Wichita, Kansas		×	×	×
	Geismar, Louisiana		×	×	×

TABLE 2 Chloromethanes Production in the United States (millions of pounds)

Year	Methyl Chloride	Methylene Chloride	Chloroform	Carbon Tetrachloride
1964	134.0	179.6	119.2	535.9
1965	187.6	210.8	152.5	593.6
1966	236.9	267.2	179.0	648.0
1967	275.6	262.3	191.0	714.0
1968	305.3	302.6	181.0	763.4
1969	391.1	360.5	216.7	876.5
1970	431.9	418.3	238.8	1,011.0
1971	437.5	401.2	230.8	1,009.2
1972	444.5	471.3	235.2	992.0
1973	544.1	520.2	252.8	1,047.3
1974	457.4	592.6	301.7	1,030.2
1975 (est.)	323.0	480.0	265.0	935.0

Methylene Chloride

Methylene chloride is used extensively as a paint and varnish remover. Its high solvency properties combined with nonflammability make it an ideal active agent for most paint and varnish removers. It is combined with F-12 fluorocarbon for a low-pressure propellant aerosol. It is also used to reduce the flammability of LPG-type propellants. Methylene chloride finds considerable use as an auxiliary blowing agent for polyether-type urethane foam systems. A growing market for this compound is as a vapor degreasing agent in the metal- and plastic-processing industries. It is particularly advantageous for cleaning products which cannot withstand the high temperatures of other degreasing chemicals such as trichloroethylene and perchloroethylene. It is used as a chemical intermediate for the manufacture of certain drugs, dyes, perfumes, chlorobromomethane, hexamethylenetetramine, and adhesives. Significant quantities are used in the manufacture of safety photographic film as a solvent wash for cellulose acetate. Other uses include general solvent for waxes, oils, and ink dyes; sterilizing agent; and food extractant solvent.

Chloroform

The use of chloroform as an anesthetic has largely been discontinued; however, some material still finds its use as an anesthetic in animal medicine. Chloroform's primary commercial use is in the manufacture of chlorofluorocarbon F-22. Many tons are consumed every year for this purpose. It serves as a reaction medium for organic syntheses. Other uses include mildew prevention on tobacco, vermicide, fungicide, and as a solvent for recovery of fatty oils, steroids, alkaloids, and glucocides. Medicinal uses include the extraction and purification of penicillin and other antibiotics and vitamins. It also finds its way into analgesic ointments, cough preparations, and toothpaste. Chloroform should never be allowed to come in contact with solid sodium hydroxide. A violent chemical reaction takes place with great evolution of heat which, if contained, can be very hazardous.

Carbon Tetrachloride

The largest single use today for carbon tetrachloride is as a precursor for chlorofluoromethane refrigerants F-11 and F-12. Considerable tonnage is used for agricultural fumigants where it is mixed with carbon disulfide, ethylene dichloride, ethylene dibromide, etc. to reduce the flammability and explosion hazard of the more active ingredients of grain fumigants. Other uses include production of organic chemicals, dyes, drugs, ore flotation, production of uranium salts, manufacture of polypropylene, and semiconductors. Carbon tetrachloride was once the principal component of fire extinguishers, but its tendency to decompose and form phosgene when sprayed into a flame has reduced this use to a low level.

Physical Properties

The chloromethanes all have a characteristic ether-like odor which is not unpleasant. All have low boiling points at atmospheric pressure, ranging from

TABLE 3 Physical Properties of Chloromethanes

	Methyl Chloride	Methylene Chloride	Chloroform	Carbon Tetrachloride
Chemical formula	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
Molecular weight	50.49	84.94	119.39	153.84
Vapor pressure at 20°C (mmHg)	3672	350	159	92
Atmospheric pressure boiling point (°C)	-23.8	39.8	61.2	76.5
Specific gravity (20°C/4°C)	0.920	1.326	1.489	1.594
Viscosity (cP) (20°C)	0.244	0.425	0.57	0.969
Latent heat of vaporization (cal/g)	102.5	78.7	59.3	46.8
Specific heat (cal/g/°C): Liquid (20°C)	0.381	0.280	0.234	0.205
Vapor (1 atm)	0.199	0.155	0.142	0.132
Thermal conductivity (Btu/h/ft ² /°F): Liquid (20°C)	0.093	0.0920	0.0751	0.0683
Vapor	.00486	0.00438	0.00455	0.00422
Critical pressure (atm)	65.9	60.9	53.8	45.0
Critical temperature (°C)	143	245	263	283
Freezing point (°C)	-97.6	-96.7	-63.5	-22.9
Flammability	Moderate	No	No	No
Explosive limits in air (% by vol.): Upper	17.2	None	None	None
Lower	8.1	None	None	None
Dielectric constant: Liquid (20°C)	12.9	9.1	4.79	2.22
Vapor	1.01	1.01	1.00	1.00
Refractive index: Liquid	1.3712	1.4244	1.4455	1.4598
Vapor (0°C)	1.00070	1.00105	1.60144	1.00180
Surface tension (dyn/cm ² , 20°C)	16.2	28.2	27.1	27
Solubility (25°C): g/100 ml in water	0.74	1.32	0.79	0.08
Water in	0.285	0.198	0.097	0.013
Heat of formation (vapor)	20.1	21.7	23.6	25.9

-23.8°C for methyl chloride to 76.5°C for carbon tetrachloride. They volatilize quite rapidly, and since their vapors have a relatively high density they tend to settle into low areas when their vapors escape. Except for methyl chloride, which is relatively stable, the molecules are subject to decomposition by hydrolysis with water, by high temperatures, oxygen, and sunlight. They have little solubility in water and are miscible with most organic liquids. Their high chlorine content gives their liquids high density and also reduces their ability to support combustion. Only methyl chloride exhibits a fire hazard.

Details of the physical properties of these chloromethanes are shown in Table 3 and in Figs. 1 through 13. The sources of these data are varied: handbooks, publications, private data, etc. Because of this wide source, no effort has been made to list references. The data are believed to be sufficiently accurate for most engineering purposes.

Table 4 gives specifications for a good grade of chloromethane products.

Handling Considerations

The chloromethanes are not among the most hazardous chemicals encountered in the chemical industry; however, one must use caution in handling them. Except for methyl chloride, they represent little or no fire hazard, but they do present toxicity problems. Most health hazards come from accidental exposure to the vapors, so proper measures must be taken to prevent accidents. Because of a high rate of volatility, small spills or leaks can result in vapors quickly encompassing a wide area. The high density of the vapors results in slow dispersal of the vapors from the spill or leak area. Good ventilation should be provided for any enclosed areas where these chemicals are used. Persons in contact with these chemicals should be given proper instruction and supervision in their handling, and a healthy respect imparted regarding their toxic properties. Generally, symptoms of overexposure to the chloromethanes are dizziness, drowsiness, incoordination, confusion, and nausea. Permanent physiological effects on the body include damage to the nervous system, liver, kidneys, and respiratory system. Flammability varies according to the chlorine content of the molecule. Methyl chloride is the most flammable, methylene chloride only very moderately flammable, and chloroform and carbon tetrachloride are nonflammable.

Methyl Chloride

Methyl chloride is moderately flammable and can form explosive mixtures in air. Its upper explosive limit is 17.2% methyl chloride by volume, and the lower explosive limit is 8.1%. Because of its high vapor pressure, it can readily escape through leaky pipe connections, valve packing glands, etc. without detection. While it has a slight ether-like odor, accumulations can occur before one is aware of the leak. Areas where methyl chloride is being handled, must be well

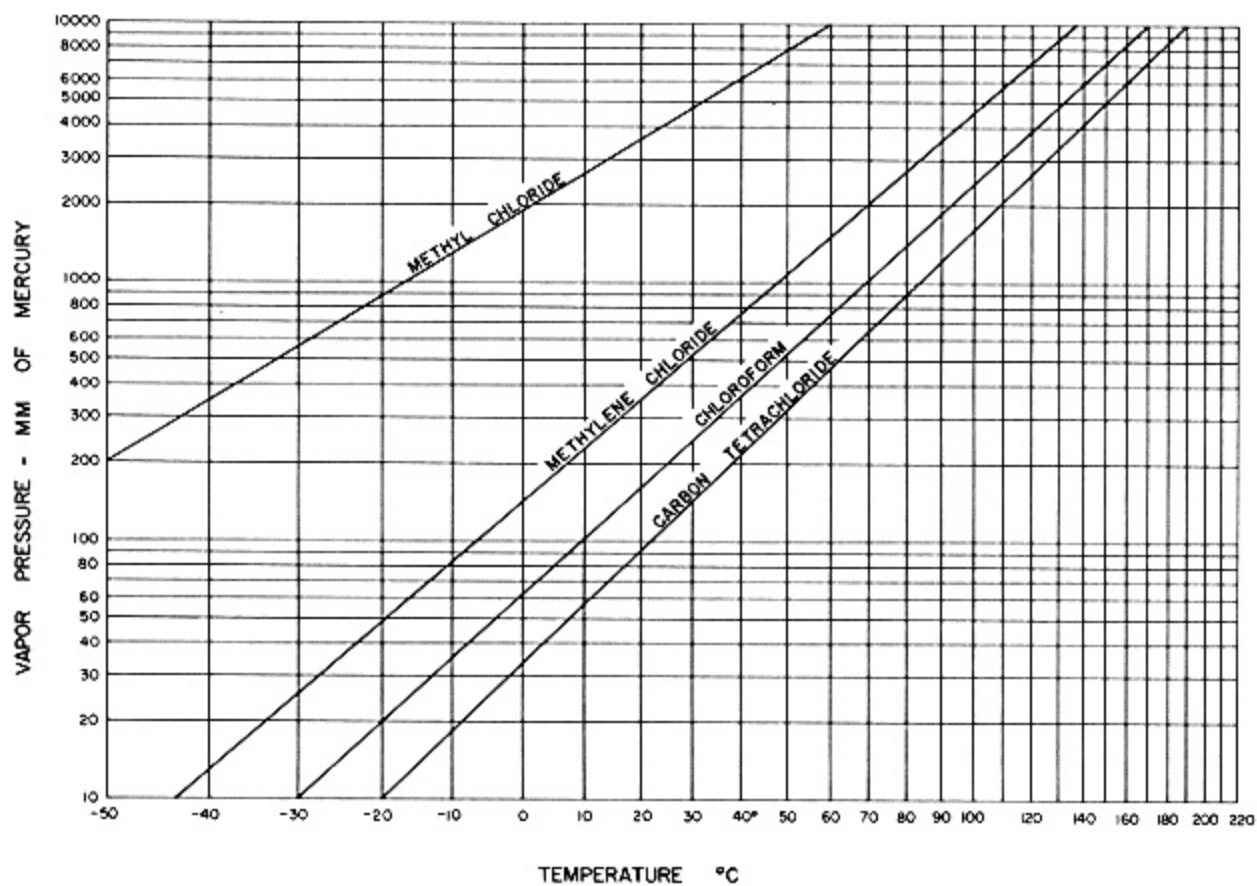


Fig. 1.
Vapor pressure of chloromethanes.

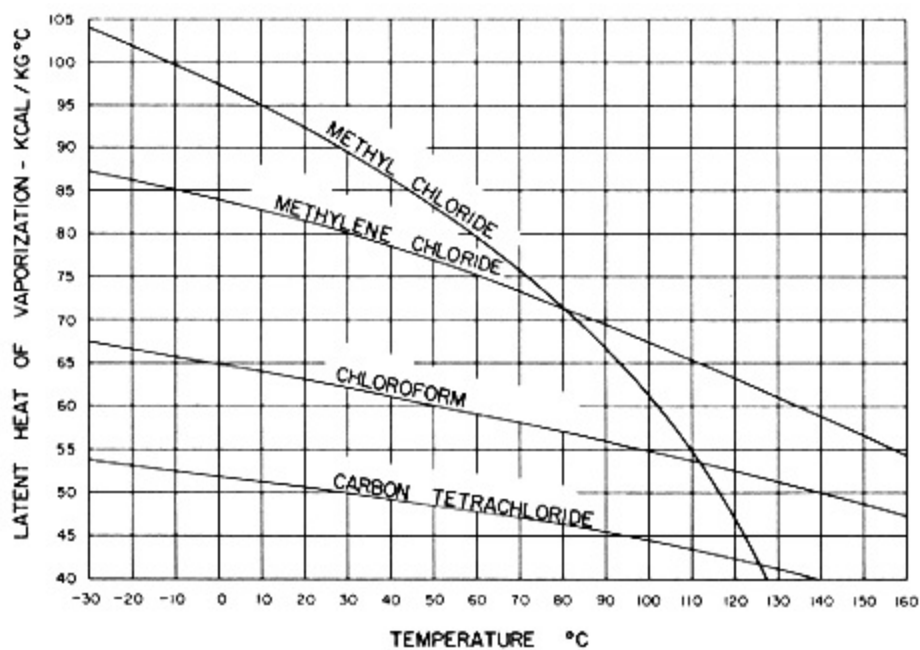


Fig. 2.
Latent head of vaporization of chloromethane liquids.

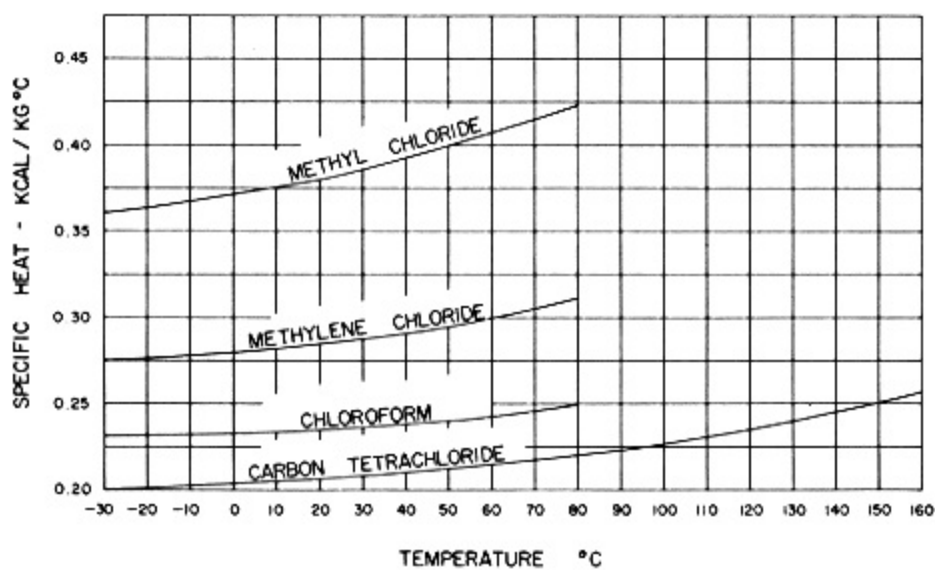


Fig. 3.
Specific heats of chloromethane liquids.

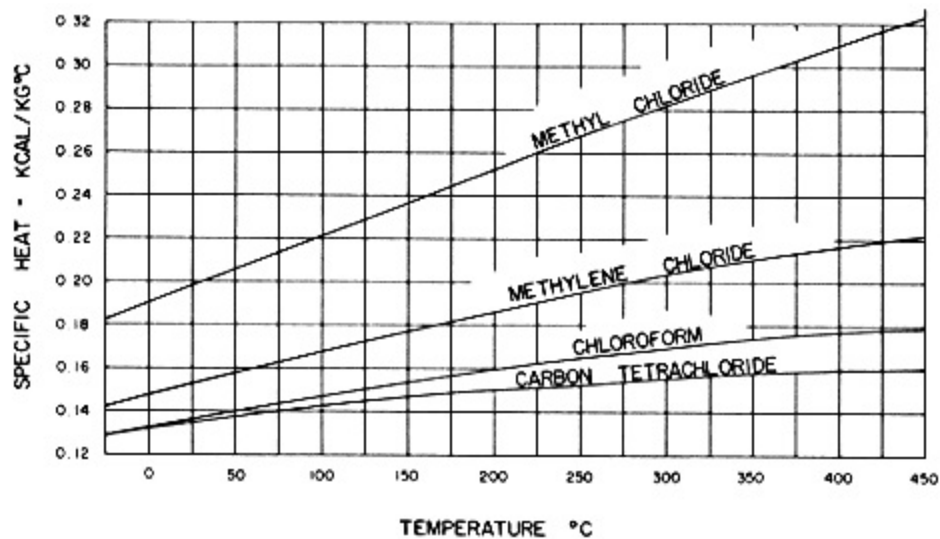


Fig. 4.
Specific heats of chloromethane vapors at 14.7 lb/in.2abs.

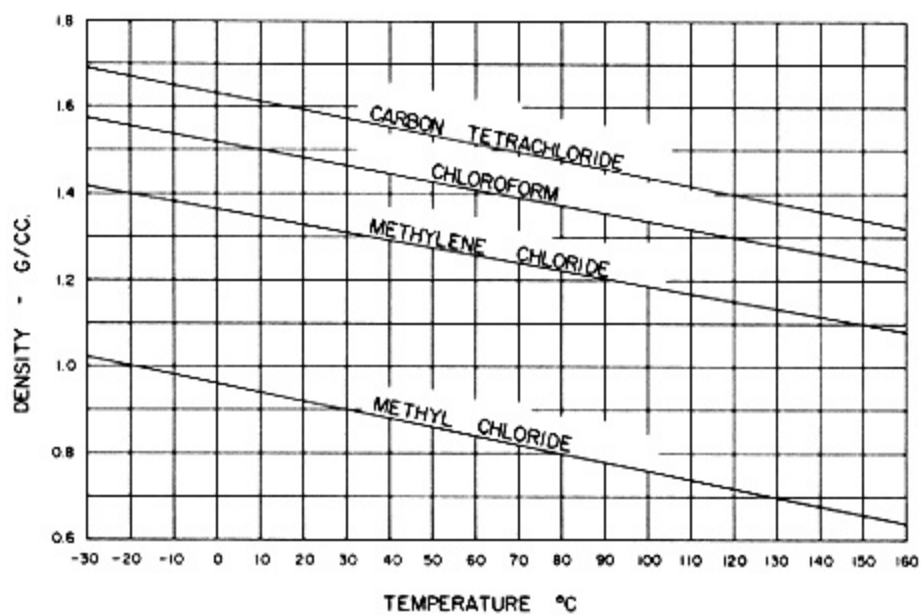


Fig. 5.
Density of chloromethane liquids.

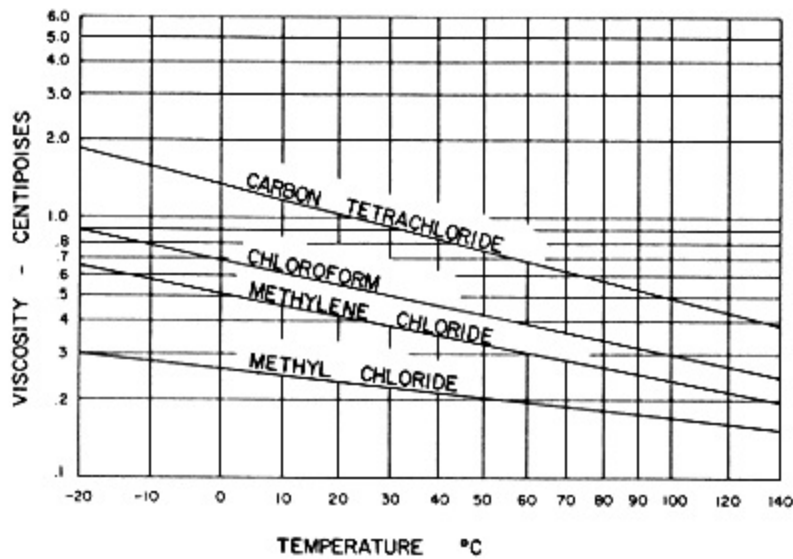


Fig. 6.
Viscosity of liquid chloromethanes.

TABLE 4 Specifications for Commercial Grade of Chloromethanes

Specifications ^a	Methylene Chloride	Chloroform	Carbon Tetrachloride	Methyl Chloride
Specific gravity (15°/4°C)	1.3301.335	1.4991.502	1.6001.607	
Color, APHA, max	10	10	10	10
Water, max ppm	100	50	50	50
Acidity, max ppm	5	0.5	1	5
Chlorine, max ppm	5	1	1	1
Residue, nonvolatile material, max ppm	10	10	5	10
Methyl chloride, max ppm	100			
Methylene chloride, max ppm		50		50
Chloroform, max ppm	50		200	10
Carbon tetrachloride, max ppm	50	50		
1,1-Dichloroethane, max ppm		100		
1,1-Dichloroethylene, max ppm	300			
1,2-Dichloroethylene, max ppm	100	100		
Trichloroethylene and heavier, max ppm			200	

ppm means parts per million by weight.

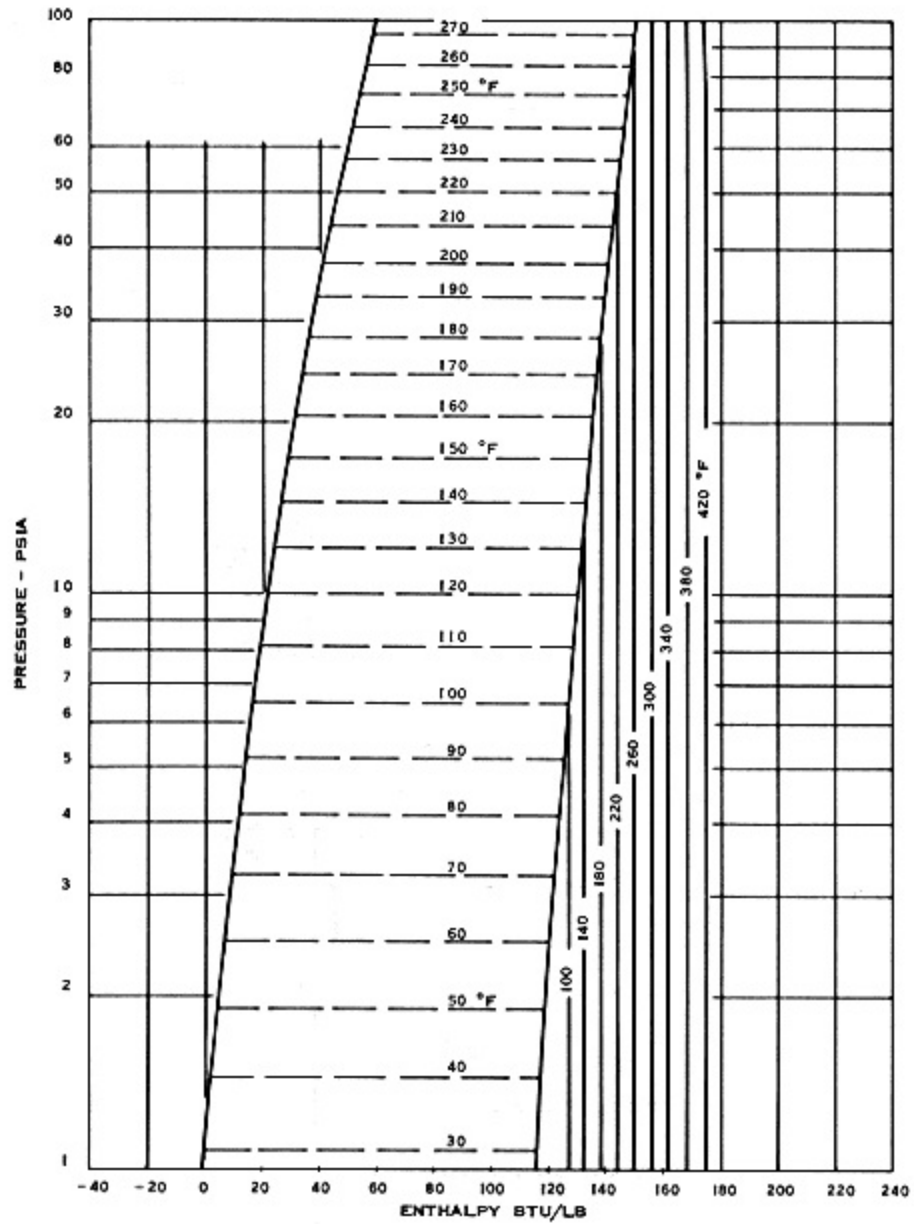


Fig. 7.
Enthalpy chart for methyl chloride.

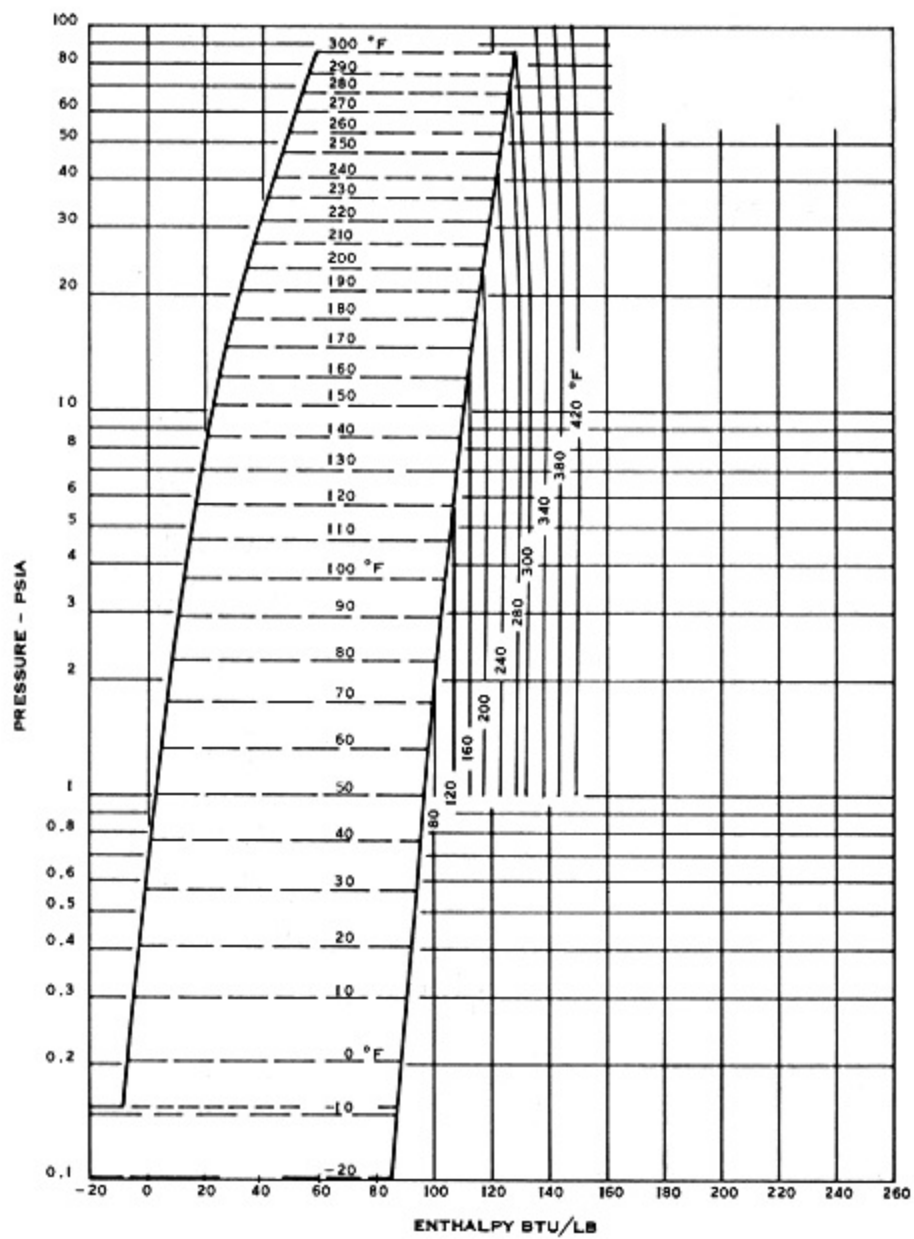


Fig. 8.
Enthalpy chart for carbon tetrachloride.

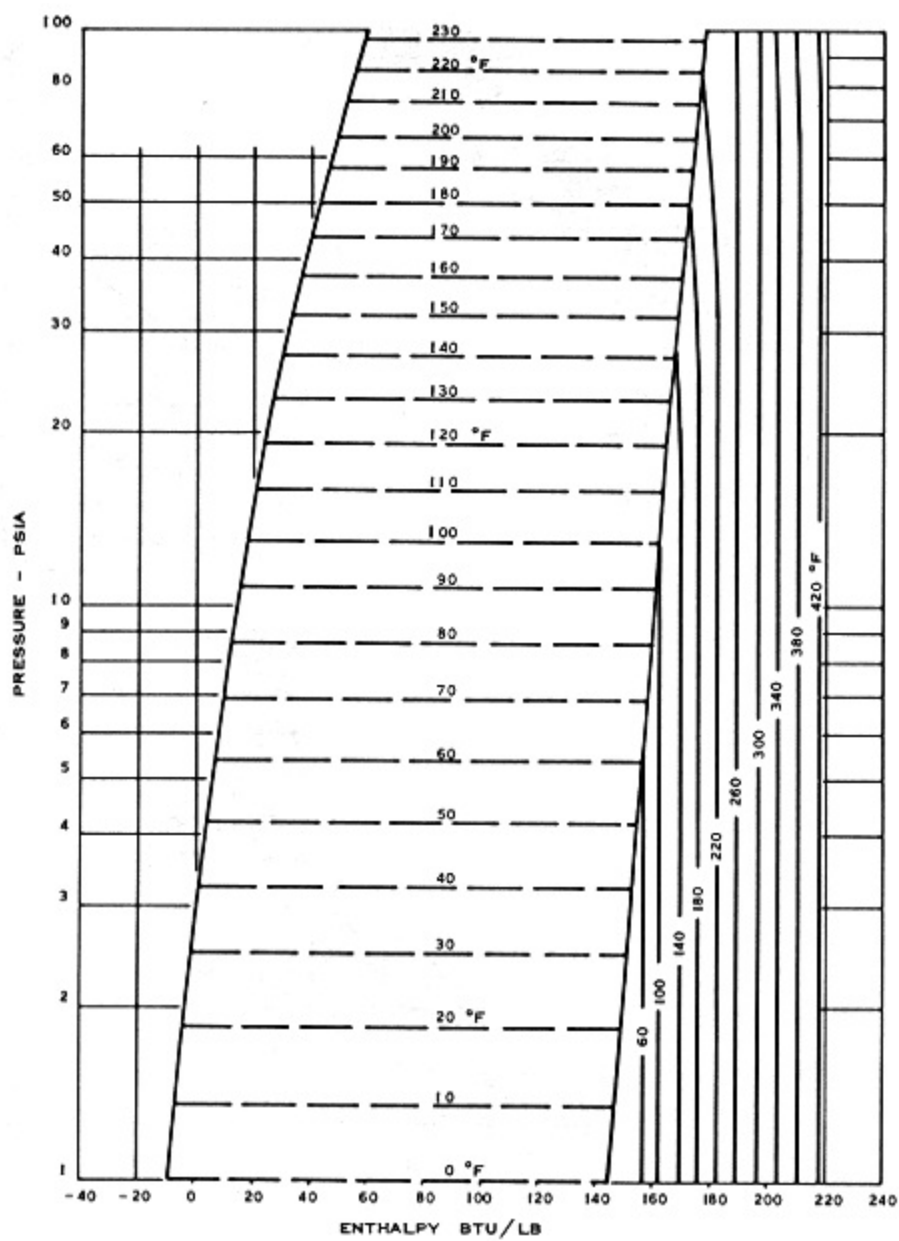


Fig. 9.
Enthalpy chart for methylene chloride.

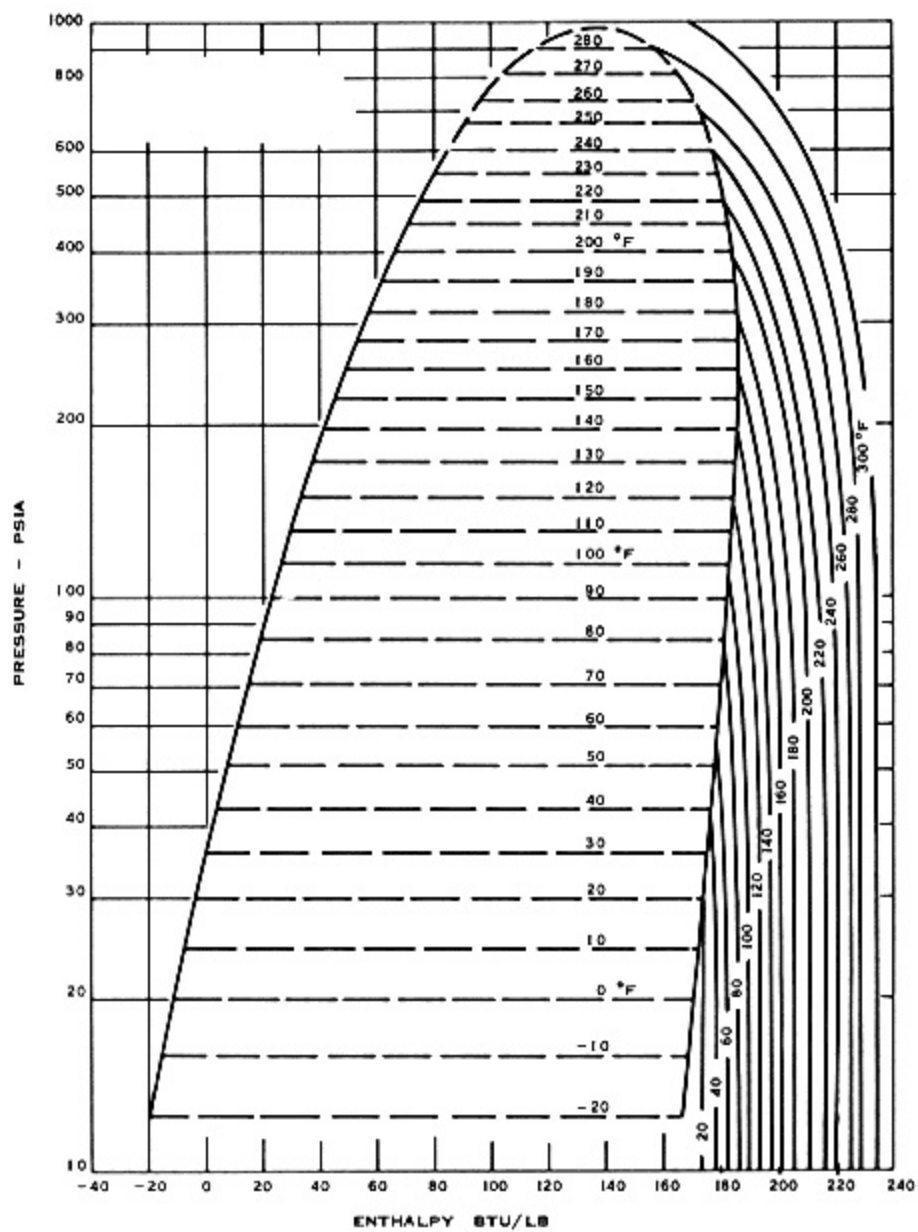


Fig. 10.
Enthalpy chart for methyl chloride.

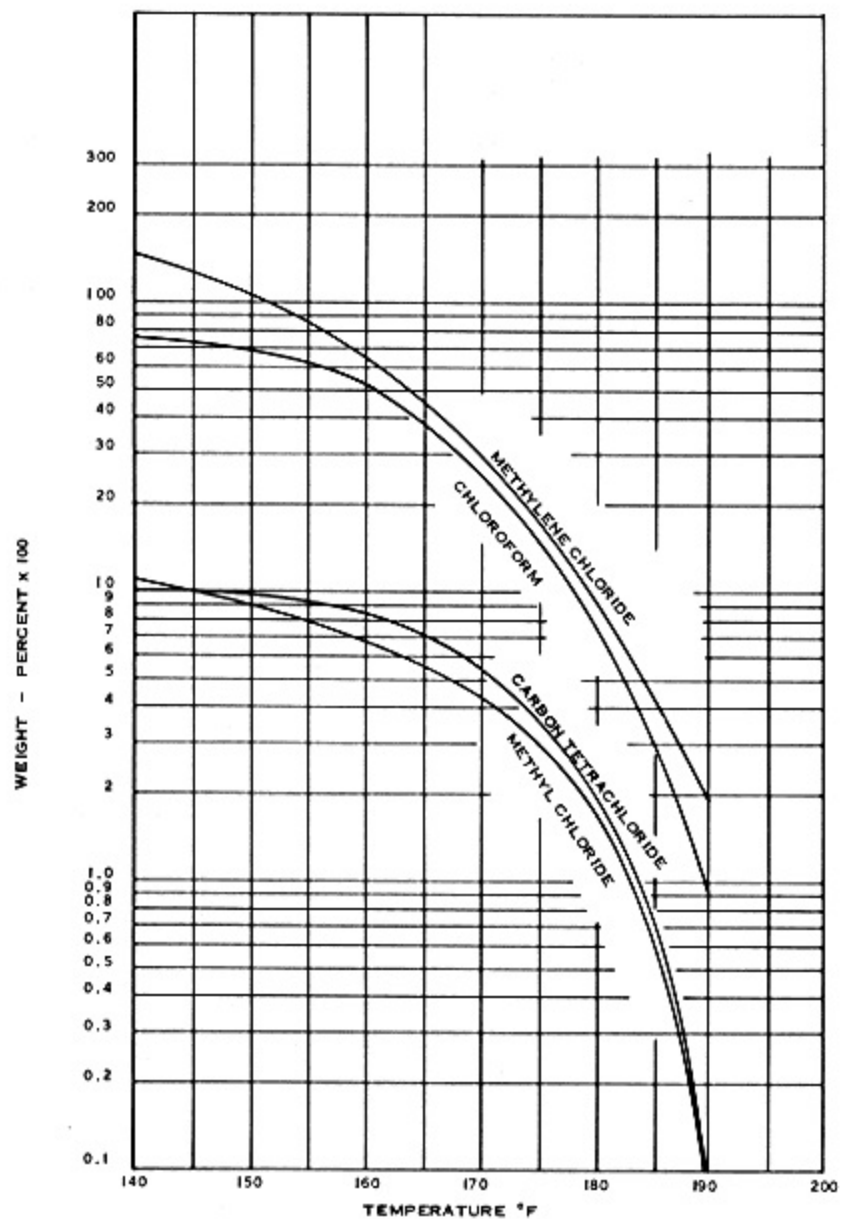


Fig. 11.
Solubility of chloromethanes in 20°Bé hydrochloric acid.

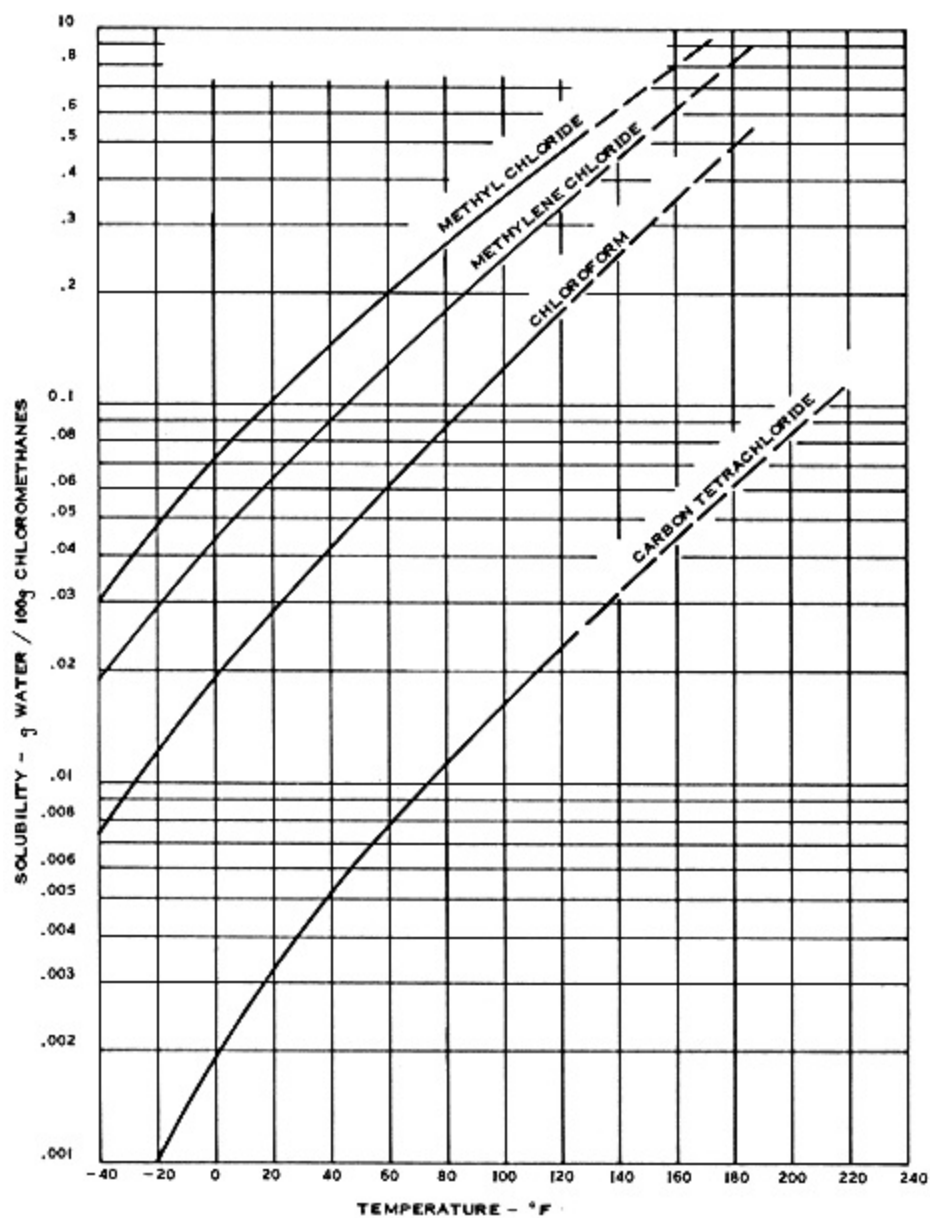


Fig. 12.
Solubility of water in chloromethanes.

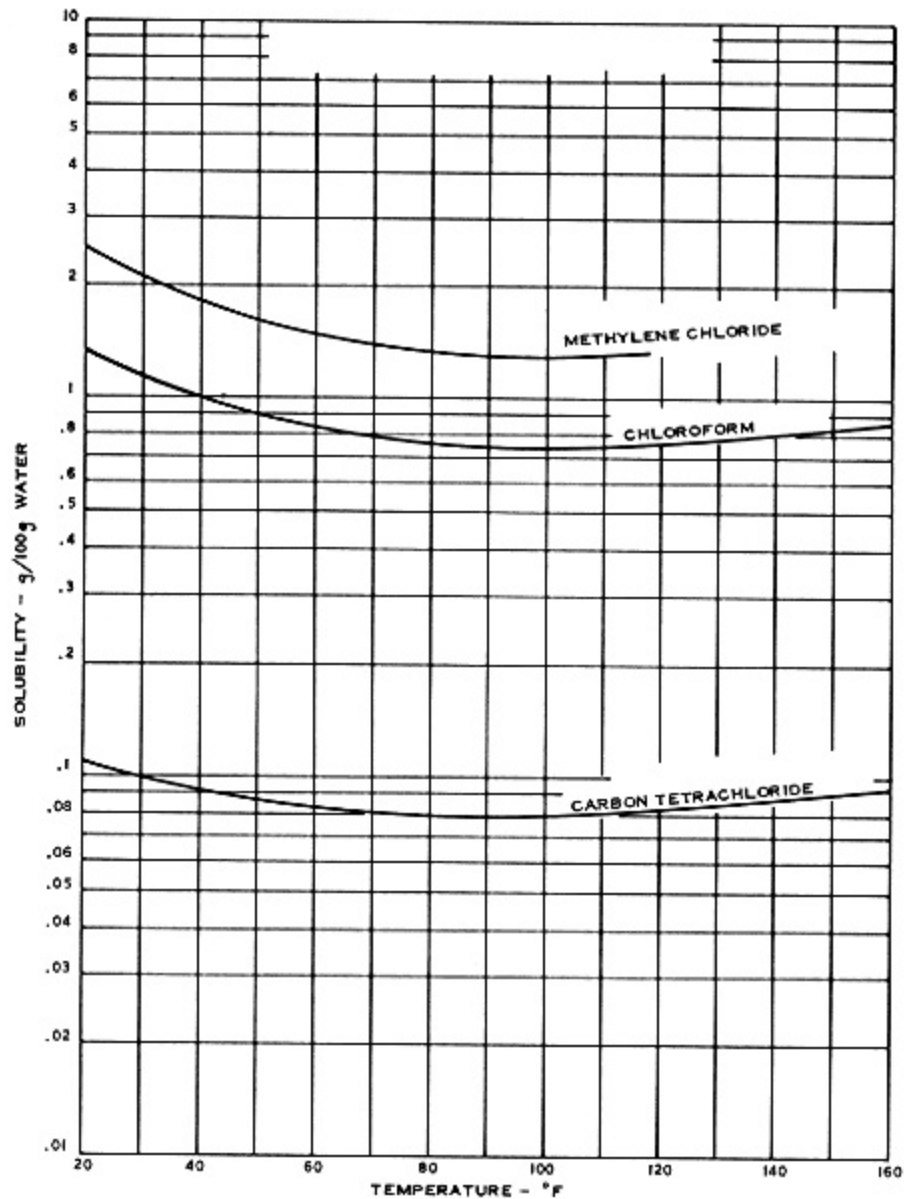


Fig. 13.
Solubility of chloromethanes in water.

ventilated. All equipment used in handling methyl chloride should be checked frequently for leaks by a halide detector or a soap solution. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a minimum safe concentration for prolonged exposure of not more than 100 ppm methyl chloride in air. Excessive exposure can result in permanent damage to the nervous system. Exposure to a 2% concentration of methyl

chloride in air for as short a time as 1 h can have serious consequences. Shipping requirements are included in the MCA warning label and IATA Red label [2]. Since methyl chloride has a positive vapor pressure at atmospheric temperatures, it must be stored as a liquefied gas under pressure in cylinders, drums, or pressurized tank cars. Steel is satisfactory for construction of the containers. Other metals are quite resistant to methyl chloride, except for aluminum. An allowance for liquid expansion in cylinders should be made, and cylinders should only be filled to about 80% of the volume of water which would normally fill the container at 40°C. Tank cars and cylinders for storage and shipping of methyl chloride generally are fitted with dip tubes which extend to the bottom of the tank or cylinder. Care should be exercised that liquid methyl chloride is not allowed to be trapped between two closed valves or else thermal expansion of the liquid can cause rupture.

Methylene Chloride

Methylene chloride is probably the least hazardous of all the chloromethanes. It is virtually nonflammable and has an ACGIH limitation for prolonged exposure of 500 ppm in air. Only an MCA warning label is required for shipment [3]. Contact with the skin should be avoided because of its tendency to dissolve out natural oils of the skin and cause dermatitis. It has powerful narcotic powers and will cause drowsiness, incoordination, and nausea from excessive exposure. Unless severe exposure has been experienced, removal to fresh air will quickly alleviate the symptoms and no permanent damage will result. While considered virtually nonflammable, methylene chloride will form an explosive mixture when mixed with high concentrations of oxygen. Pure methylene chloride is subject to hydrolysis in the presence of water. For this reason it must either be kept free from contact with moisture or be specifically inhibited against water hydrolysis. Even though inhibited, it is a good idea not to allow water accumulations in methylene chloride storage. While the vapor pressure of methylene chloride is generally below that of atmospheric pressure in most storage conditions, precautions should be taken to prevent storage containers from becoming overheated by exposure to sunshine. Because of its susceptibility to hydrolysis from water, storage tanks preferably should be blanketed with dry air or dry nitrogen. For critical uses, storage tanks containing methylene chloride should be equipped with devices for drying atmospheric air which breathes into the tank due to changes in atmospheric temperatures. Storage and shipping containers can be made of mild steel. For critical uses, drums should preferably be galvanized or lined with a phenolic coating. The liquid should be kept free of contact with metal chlorides and oxides, particularly ferric compounds because they tend to promote decomposition.

Chloroform

Chloroform is nonflammable and will not form explosive mixtures at normal atmospheric temperatures and pressures. However, if subjected to high

temperatures, such as a flame, it will burn and give off toxic gases. The principal hazard in handling chloroform is its narcotic effect on the human body. While formerly used as an anesthetic, overexposure can cause severe damage to the respiratory system, heart, and liver. It is for this reason that its use as an anesthetic has been discontinued. Acceptable exposure limits in air by ACGIH is 50 ppm. Exposure to as much as 2000 ppm can cause symptoms of drowsiness, dizziness, confusion, and nausea. The liquid can be very harmful if swallowed and will cause skin and eye irritations. Manufacturing Chemists' Association Data Sheet No. SD-89 should be consulted for more details on the handling and shipping of chloroform [4]. Pure chloroform is quite unstable to moisture, sunlight, and oxygen of the air. It is virtually impossible to store pure chloroform for any period of time without decomposition occurring. For this reason, the commercial material always contains stabilizers. Even so, precautions must be taken in handling chloroform if it is to retain compliance to specification. Small containers should be kept sealed and any glass bottles should be amber colored. For large storage vessels, mild steel is satisfactory; however, it must be kept free of rust and any ferric chloride accumulations. A new storage tank should be sandblasted before the introduction of chloroform. Storage tank vents should be equipped with a breather system which will dry air breathing in and out of the tanks. For critical uses, drums should be either galvanized or lined with a phenolic coating. For pharmaceutical grades, containers generally are tinned. Chloroform should not be allowed to come in contact with aluminum or alkali metals, and should never be allowed to come in contact with solid sodium hydroxide. A violent chemical reaction takes place with great evolution of heat which, if contained, can be very hazardous. Calcium chloride should be used as a drying agent for removal of any moisture in the chloroform.

Carbon Tetrachloride

Carbon tetrachloride presents no hazard from the viewpoint of flammability and explosion. This property has often been utilized by mixing carbon tetrachloride with other more hazardous chemicals to reduce explosion limits. Hazard from carbon tetrachloride is largely that of its high toxicity. Prolonged exposure to small amounts can cause serious damage to the liver. Ingestion of small amounts can produce severe physiological effects. The presence of alcohol in the blood will intensify the effects of exposure to CCl_4 . Because it can be absorbed through the skin, contact with the liquid should be avoided. ACGIH acceptability in air for prolonged exposure is 10 ppm. Shipment requires an MCA warning label and an IATA poisonous label [5]. Carbon tetrachloride has been banned by the U.S. Food and Drug Administration for any products intended to be used in the home. It is relatively stable when stored dry and in the absence of sunlight. Commercial grades rarely contain inhibitors; however, because inhibitors are not added, caution must be taken in storage and shipment of the chemical. It must be kept free of moisture, particularly at elevated temperatures which can cause rapid decomposition. For this reason, closed containers should be used, and storage tanks should have vents which

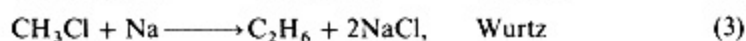
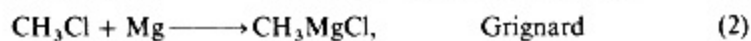
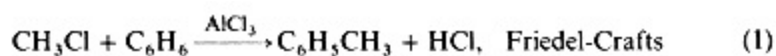
will dry air breathed into the vapor space. Mild steel is satisfactory as a material of construction; however, it should be free of rust. A new tank should be sandblasted and all accumulations of ferric oxide removed before introduction of carbon tetrachloride. Metal chlorides also tend to promote decomposition, particularly ferric chloride. Drums for shipping can be carbon steel and need not be galvanized or plastic-lined, provided they are free of rust when filled. Carbon tetrachloride should not be subjected to temperatures above 400°F because phosgene will result.

Chemical Reactions of Chloromethanes

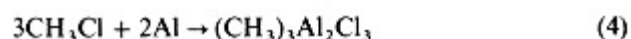
Methyl Chloride

Methyl chloride chlorinates quite readily to form the other three chloromethanes: methylene chloride, chloroform, and carbon tetrachloride. This can be done either thermally or by photochemical means, as discussed elsewhere. Many tons of methyl chloride are used for this purpose each year. Generally, the methyl chloride used for this purpose is manufactured integrally with the other chloromethanes.

Methyl chloride has the ability to furnish methyl groups for methylations in the Friedel-Crafts reaction, Grignard reagent, and Wurtz synthesis. Typical examples of these reactions are as follows:



Methyl chloride will react vigorously with aluminum to produce methyl-aluminum sesquichloride which is a catalyst for polymerizations and hydrogenation of hydrocarbons:



Silicon will react with methyl chloride in the presence of copper to form dimethyldichlorosilane:

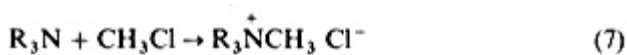


This reaction is an intermediate step in the preparation of silicones.

Tetramethyl lead, used as a gasoline additive, is made by the reaction of methyl chloride with monosodium lead alloy. Aluminum chloride is used as a catalyst for the reaction:

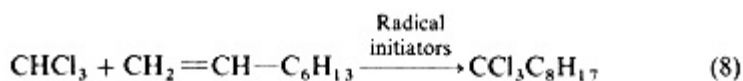


Methyl chloride will react with a tertiary amine to form quaternary ammonium chloride:



These compounds are important in the production of special detergents, fungicides, disinfectants, etc.

Chlorine can be introduced into a long-chain hydrocarbon molecule by the reaction of methyl chloride with primary olefins [6]:

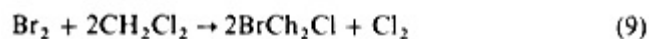


Methylene Chloride

Methylene chloride will enter into many of the same reactions as methyl chloride, but the reactions are slower and complex mixtures develop. As a result, methylene chloride is seldom used for the manufacture of other chemicals where its molecule enters into a chemical reaction. Its use is largely that as a solvent or other uses where its physical properties are advantageous. Its principal chemical reaction of commercial use is its ability to chlorinate further to chloroform and to carbon tetrachloride. It reacts with aluminum and will react violently with alloys of potassium and sodium.

Methylene chloride hydrolyzes with water to produce phosgene and chlorine. For this reason, commercial methylene chloride contains inhibitors.

Bromochloromethane results from the reaction of bromine and methylene chloride:



This is an important reaction in chloromethanes manufacture, as any bromine in the chlorine will thus react and result in an impurity in the product.

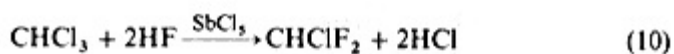
Chloroform

Like methyl chloride and methylene chloride, chloroform can be further chlorinated, the result being carbon tetrachloride; however, the reaction is slower than any of the other chloromethanes chlorinations. It is difficult to drive totally to carbon tetrachloride when feeding a mix of lighter chloromethanes to a chlorination reactor.

Chloroform will react quite strongly with solid caustic soda. Care should be taken not to mix chloroform with NaOH because the reaction can become uncontrollable, resulting in an accident. The reaction that takes place produces unstable intermediate compounds which can undergo aldol condensations and/or produce CO and HCl [79]. Chloroform is the only chloromethane which will undergo such a reaction with NaOH. The other chloro-

methanes can safely be mixed with caustic soda, which is often used as a drying agent for these chemicals.

The most important chemical reaction of chloroform is that with HF to produce fluorocarbons. Antimony pentachloride is used as a catalyst:



Chlorodifluoromethane, better known as Fluorocarbon Type "22," is used extensively as a refrigerant and accounts for 80 to 90% of the industrial consumption of chloroform. This fluorocarbon is also used for the manufacture of tetrafluoroethylene which in turn is polymerized to Teflon and Kel-F plastics. Chloroform can also be made to yield dichlorofluoromethane and trifluoromethanes, but these are of little or no industrial importance.

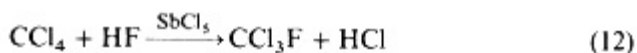
Chloroform will react with bromine to form the bromochloromethanes CCl_3Br , CCl_2Br_2 , and CClBr_3 . It will not react with iodine.

Chloroform will react with amines in an alcoholic alkaline solution to form isonitriles. The reaction with aniline results in phenyl isonitrile which has a very strong characteristic odor and is used as a test for the presence of amines:

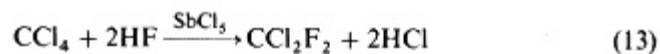


Carbon Tetrachloride

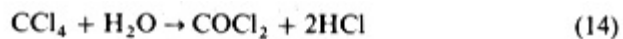
Like chloroform, carbon tetrachloride will react with HF to produce chlorofluoromethanes. This is by far the most important use of carbon tetrachloride, as it is by this reaction that Type F-11 and F-12 refrigerants are produced. For F-11:



and for F-12:



Important in the manufacture of chloromethanes is the reaction of CCl_4 with water to produce CO_2 , phosgene, and HCl. At elevated temperatures, as encountered in the reboilers of distillation columns, the reaction will proceed rapidly should a steam leak occur into the process side of the tubular:



Carbon tetrachloride will enter into a limited number of other chemical reactions which are of no importance industrially. A good textbook on organic chemistry should be

consulted for these reactions.

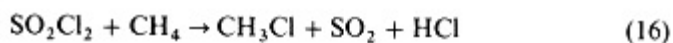
Manufacturing Methods

Indirect Chlorination Methods

A number of chemical methods for the preparation of chloromethanes are presented in the various organic chemistry textbooks, reference works, and patent literature available on the library shelves. These generally suggest the substitution, by one means or another, of a chlorine atom for the hydrogen on the methane molecule. Most of these methods are not very practical and few, if any, have been used commercially for any extended period of time. However, it may be worthwhile to present the chemistry of some of these methods.

Chlorination by Sulfuryl Chloride (SO₂Cl₂)

Sulfuryl chloride can be utilized as a chlorinating agent to substitute hydrogens on the methane molecule.



The methane is preheated to a temperature above 200°C and bubbled through SO₂Cl₂ where a substitution chlorination reaction takes place. The resulting SO₂ is then reacted with elemental chlorine to produce more SO₂Cl₂. Little net heat of reaction is involved, and the reaction takes place without the "explosive" conditions resulting from direct mixing of methane and chlorine. Yields as high as 50% chloroform from methane are reported [10].

A modification of this method [11] is the addition of SO₂ to a vapor-phase chlorination medium. Undoubtedly, the SO₂ modifies the Cl₂ and results in a controlled reaction.

Antimony Pentachloride

In this method, antimony pentachloride is the carrying agent of chlorine to be substituted in the methane molecule:



Liquid antimony pentachloride flows countercurrent to a gas stream of methane over quartz particles impregnated with cuprous chloride. The reaction is carried out at 300°C.

Phosphorus Pentachloride

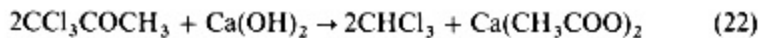
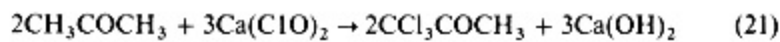
Phosphorus pentachloride will serve as a chlorinating medium for chlorine and methane. At high temperatures, chlorine is liberated to react with the

methane. A continuous feed of chlorine to the system maintains the level of PCl_5 content in the reacting medium:



Chloroform from Acetone

Chloroform can be produced by reacting acetone with calcium hypochlorite. The intermediate product is trichloroacetone which is reacted with lime to produce chloroform and calcium acetate. The original chlorine enters the system in the chlorination of calcium hydroxide to calcium hypochlorite. This is an expensive method of making chloroform, but it has been manufactured by this method.

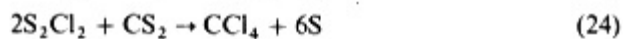


Ferric Chloride

A number of patents [1215] have been issued covering chlorination of hydrocarbons utilizing ferric chloride as the modifying agent for reaction of chlorine with hydrocarbon molecules. An interesting patent [16] was issued to Sun Research & Development Co. in which hydrogen chloride and oxygen, along with methane, are fed to a fluid bed of ferrous chloride. The ferrous chloride is converted to ferric chloride which vaporizes at the temperature maintained in the reactor chamber. The vapor, as ferric chloride, chlorinates the hydrocarbon and in turn is converted back to solid ferrous chloride which falls back into the fluid bed. This method has not been used commercially, but it has interesting aspects.

Carbon Tetrachloride by Carbon Disulfide

Many tons of carbon tetrachloride are made by the reaction of chlorine with carbon disulfide:



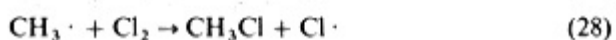
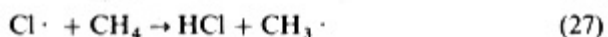
This is a practical and economical method for manufacturing carbon tetrachloride and is practiced extensively throughout the world. More details on this technology are given below.

Direct Chlorination of Methane

Introduction

Many of the chemistry textbook references on library shelves indicate that direct chlorination of methane for the manufacture of chloromethanes is very difficult. However, except for carbon bisulfide for carbon tetrachloride manufacture, thermal chlorination of methane or methyl chloride is the most direct and economical method for the manufacture of chloromethanes and today is the method most commonly practiced throughout the world. Early investigators, in the late 1930s, recognized that direct methane chlorination would be the best route to the chloromethanes if some of the problems associated with direct chlorination could be solved, not the least of which were explosions and carbon liberation in the chlorination reaction. These and other problems were solved in the 1940s, and many plants have since been built.

Under the proper conditions, chlorine will readily react with methane or its partially chlorinated derivatives. This is accomplished by activating the chlorine molecule so it will disassociate to atomic chlorine and attack the methane molecule, replacing its hydrogen atoms. Chlorine can be activated in one of two ways: elevated temperature or actinic light radiating in the range of 3000 to 5000 Å units. The chlorine molecule is disassociated to two atoms of chlorine ($\text{Cl} \cdot$) which are very active and will replace hydrogens on a methane molecule. Investigators agree that the chlorination proceeds by a chain reaction. When the methane molecule is attacked by a chlorine atom, a hydrogen chloride molecule is formed along with an organic-free radical. This radical then reacts with an undisassociated chlorine molecule, generating additional chlorine atoms perpetuating a reaction chain and producing a chloromethane molecule:



This chain reaction tends to be terminated by the reactions



The chain reaction can also be terminated by the presence of certain impurities such as oxygen. If the chain reaction is not terminated, then a large number of chlorine molecules can be made to react as a result of the original disassociation of but a single chlorine molecule. Thus, with a strong activation of the chlorine, such as high temperature or strong actinic light, a mass of mixed vapors can be made to react rapidly to the complete exhaustion of the lessor compound in the reacting mass. However, at lower temperatures or limited light energy input, impurities such as oxygen or other chain-terminating impurities can hinder the reaction and make it difficult, or impossible, to drive to

completion. Pease and

Walz [17] studied the effect of oxygen on termination of the chain reaction of methane chlorination. They found that the presence of 1.25% oxygen in the methane decreased the rate of chlorination of methane tenfold in the temperature range of 250°C. However, they also found that the temperature coefficient of oxygen inhibition was found to be at least twice that of the uninhibited reaction. Thus, in the 350 to 450°C range, small concentrations of oxygen had a relatively negligible inhibiting effect. However, experience in thermal chlorination of methane has been that relatively pure compounds should be used for a successful thermal chlorination process. The chlorine supply must be liquid chlorine as normally produced in a well-designed chlorine liquefaction plant. Cell gas cannot be made to work successfully in an activated light chlorination process and only with difficulty in a thermal process. A commercial process is known where a successful pilot plant operation was followed by a commercial unit built exactly like the pilot plant, but the reactor would not work satisfactorily. Chlorine and hydrocarbon passed through the reactor relatively unaffected. Investigation showed the difficulty was entirely due to the difference in chlorine purities used in the pilot plant and the commercial unit. The commercial reactor was very successful when high-purity chlorine was provided as feed to the reactor system.

While a temperature of about 275°C is sufficient to produce disassociation of chlorine and initiate a chlorination reaction, it has been found in commercial operations that an operating temperature in the range of 400 to 450°C is necessary to have a stable, self-sustaining reaction. Undoubtedly, the higher temperature is very instrumental in overcoming the effects of relatively small impurities in the feeds. It is not desirable to go to temperatures much above 450°C because of other problems associated with the reaction such as by-product reactions and ignition of the reacting compounds. Theoretically, ignition would not occur if the heat of reaction could be removed fast enough. However, as the temperature of the reacting gases increases, the rate of reaction is accelerated beyond any means possible to remove the heat fast enough to carbon. The chlorine and hydrogen all go to HCl:



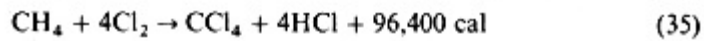
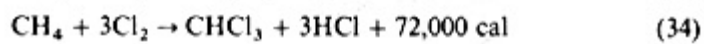
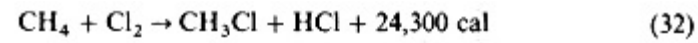
This reaction liberates a vast amount of heat and, once started, is impossible to control. Thus the explosions reported in many textbooks. Commercial operations sometimes experience this pyrolysis if not properly designed or if the means used for heat control suddenly fails. Explosions can occur, but commercial reactors are equipped with rupture disks to release the pressure surge.

Chemistry and Kinetics of Methane Chlorination

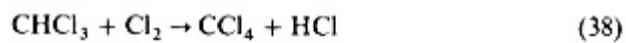
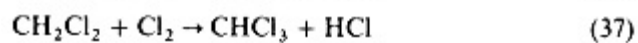
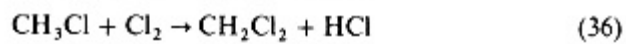
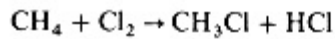
The chemistry and basic kinetics of methane chlorination are believed to be the same whether the reaction takes place in the liquid or vapor phase under the influence of actinic light, or in the vapor phase by high temperature activation.

Therefore, the following discussion is basic to all three methods of methane chlorination.

The chlorination of methane can be represented by



The first three products of chlorination—methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), and chloroform (CHCl_3)—are each themselves subject to further chlorination to the succeeding heavier chloromethane compound. This means that when methyl chloride is formed, some of it will also be further chlorinated in the same reaction mass to methylene chloride. Similarly, some methylene chloride also will be chlorinated to chloroform, and some chloroform to carbon tetrachloride. The chlorination of methane can therefore also be represented by



The products of chlorination of methane are therefore both a polysubstitution and a monosubstitution even when low ratios of chlorine to methane are used in the initial feed gases. The final product distribution of the chloromethanes in the reaction mass when all the chlorine has been reacted relative rates to each other at which each compound is subject to chlorination. These reactions have a very high activation energy (about 30,000 cal) and generally are considered to be irreversible.

McBee, Hass, and their co-workers were early investigators of the chlorination of methane, and their paper [18] is one of the classics in the literature of hydrocarbon chlorination. In their paper they presented a set of curves showing the distribution of products from methane chlorination at various chlorine-to-methane feed ratios. Their data are reproduced in Fig. 14. Hirschkind [19] later reported confirming data in the first paper on chlorination presented by an industrial organization commercially engaged in the manufacture of chloromethanes.

The McBee reactor was a length of 1/4-in. nickel pipe with methane fed into the front end and successive injections of chlorine added at intervals along the pipe reactor. With this small-size reactor and multiple injection points, it is probably safe to assume the McBee data represents a plugflow-type reaction with about as little backmixing of the reaction products during the chlorination reaction as could practically be achieved. The product distribution

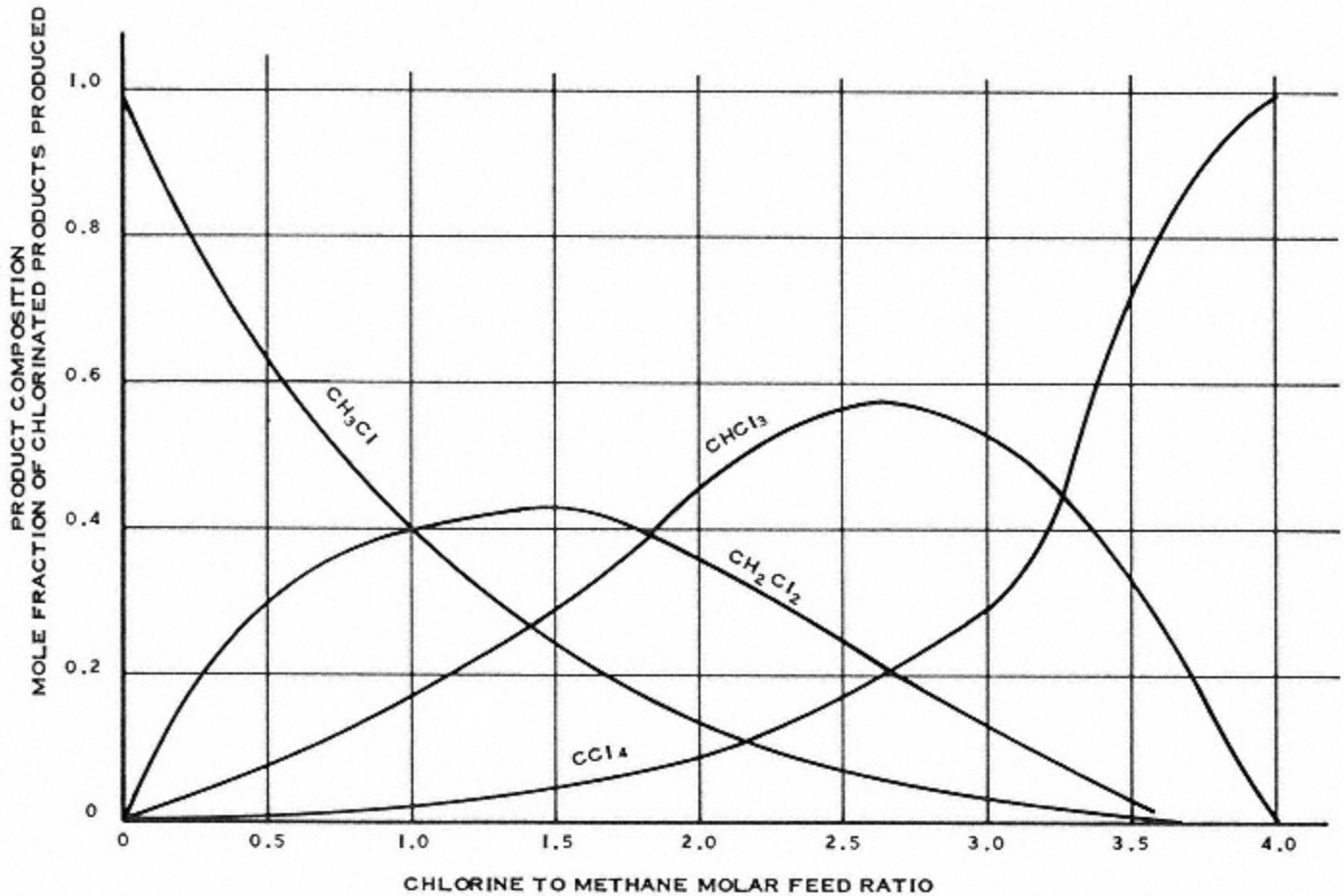


Fig. 14.
Experimental product distribution for methane chlorination [18].

data, within the accuracy of the experimental methods used, represent about the ultimate one could expect in product distribution favoring monosubstitution.

McBee and his co-workers did not present kinetic data from their work. However, it is possible to use the experimental results to calculate the reaction rate constants [20] for the chlorination of methane and partially chlorinated methanes. These data are shown in Fig. 15.

It is possible, by using relative reaction rate data, to mathematically calculate a set of product distribution curves similar to those arrived at experimentally by McBee [2024]. Derivation of the equations for these curves are quite complex (interested persons may consult the references) and will not be presented. However, the results of these mathematical gymnastics are useful and are as follows:

$$\frac{C_3}{C_{2_0}} = \frac{C_{3_0}}{C_{2_0}} \quad \phi^a + A\phi - A\phi^d \quad (39)$$

$$\begin{aligned} \frac{C_4}{C_{2_0}} &= \frac{C_{4_0}}{C_{2_0}} \quad \phi^b + Z \frac{C_{3_0}}{C_{2_0}} (\phi^b - \phi^a) + B\phi + D\phi^a \\ &= (B + D)\phi^b \end{aligned} \quad (40)$$

$$\begin{aligned} \frac{C_5}{C_{2_0}} &= \frac{C_{5_0}}{C_{2_0}} \quad \phi^d + Y \frac{C_{4_0}}{C_{2_0}} (\phi^d - \phi^b) + X \frac{C_{3_0}}{C_{2_0}} (\phi^a - \phi^d) - W \frac{C_{3_0}}{C_{2_0}} (\phi^b - \phi^a) \\ &\quad + E\phi - F\phi^a + G\phi^b - (E - F + G)\phi^d \end{aligned} \quad (41)$$

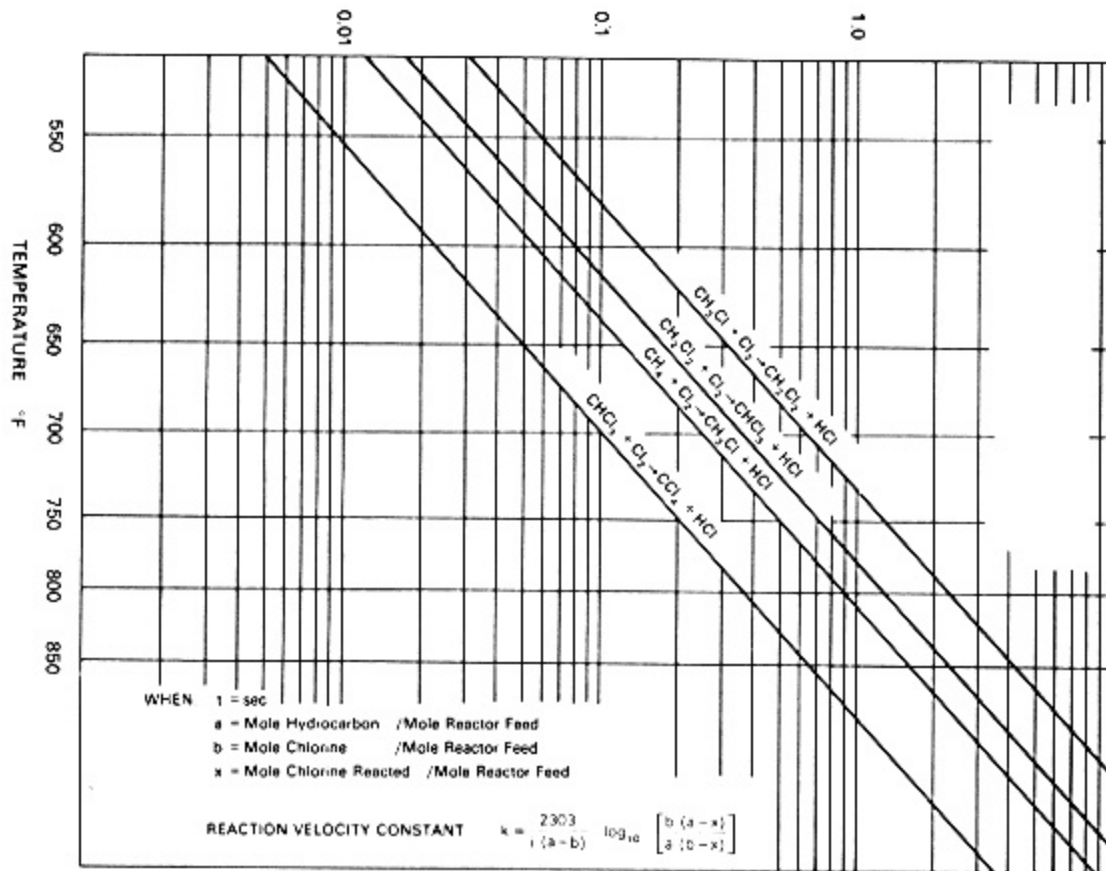


Fig. 15.

Reaction velocity constants for methane chlorination at a feed ratio of $\text{Cl}_2/\text{CH}_4 = 1.1$ [18].

Where Subscripts 1,2,3,4, and 5 refers to chlorine, methane, methyl chloride, methylene chloride, and chloride, and chloroform, respectively

Subscript 0 refers to the initial concentration

C represents the molar concentration of the component

K is the reaction constant from Fig. 15.

$$\phi = C_2/C_{20}$$

$$a = K_2/K_1$$

$$b = K_3/K_1$$

$$d = K_4/K_1$$

$$A = 1/(a - 1)$$

$$B = aA/(b - 1)$$

$$D = dA/(d - b)$$

$$E = bB/(d - 1)$$

$$F = dD/(a - d)$$

$$G = \frac{b(B + D)}{b - d}$$

$$T = \frac{ad}{(a - b)(b - d)}$$

$$U = \frac{bd}{(a - b)(a - d)}$$

$$V = d/(b - d)$$

$$W = \frac{ab}{(a - b)(b - d)}$$

$$X = \frac{ab}{(a - b)(a - d)}$$

$$Y = b/(b - d)$$

$$Z = a/(a - b)$$

An equation for carbon tetrachloride can be derived, but the complexity makes it much easier to arrive at carbon tetrachloride concentrations by using a carbon balance. The initial chlorine can be arrived at by a chlorine balance. These equations have been used to calculate product distribution curves as shown in Fig. 16. The results agree quite well with McBee's experimentally

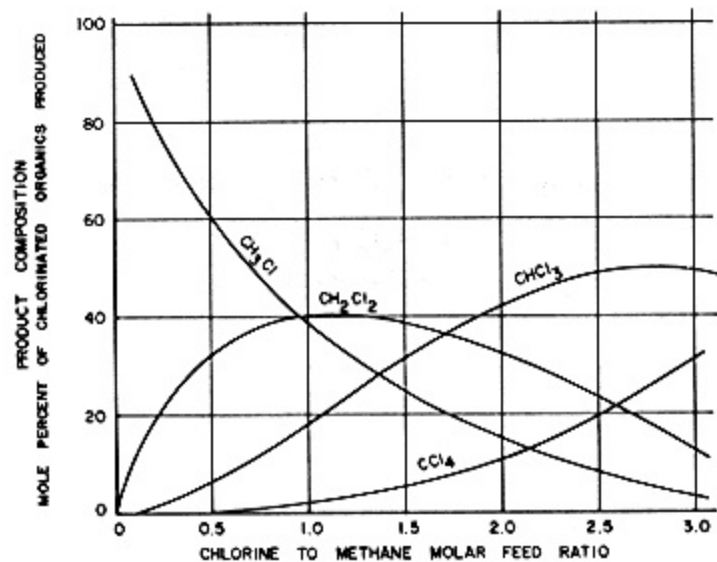


Fig. 16.
Methane chlorination product distribution from plugflow reactor reaction rate constants from McBee data [18].

derived curves. Because of experimental errors and difficulty of chemical analysis in the days of McBee's work, the mathematically derived curves may be more accurate than those of McBee.

In actual practice of methane chlorination, a commercial reactor probably will have sufficient backmixing of the reactants that the product distribution will not follow the curves developed for a plug-type flow. One known commercial reactor built in 1956, which was basically a scale-up the McBee lab unit, gave results more closely approaching a backmixed reactor than a plugflow type. Most commercial reactors today probably have an even greater tendency toward backmixing.

For a completely mixed reactor, a different approach must be taken from that of a plug-type flow unit. The composition for a given compound in the product is equal to its composition at any point in the reactor. The rate of appearance or disappearance of a compound is then the same at all points in the reactor and is constant. A series of equations corresponding to Eqs. (39), (40), and (41) can be mathematically developed for a backmixed reactor:

$$\frac{C_3}{C_{20}} = \frac{\phi + \frac{\phi}{1-\phi} \frac{C_{30}}{C_{20}}}{\frac{\phi}{1-\phi} + \frac{K_2}{K_1}} \quad (42)$$

$$\frac{C_4}{C_{20}} = \frac{\frac{K_2}{K_1} \frac{C_3}{C_{20}} + \frac{\phi}{1-\phi} \frac{C_{40}}{C_{20}}}{\frac{\phi}{1-\phi} + \frac{K_3}{K_1}} \quad (43)$$

$$\frac{C_5}{C_{20}} = \frac{\frac{K_3}{K_1} \frac{C_4}{C_{20}} + \frac{\phi}{1-\phi} \frac{C_{50}}{C_{20}}}{\frac{\phi}{1-\phi} + \frac{K_4}{K_1}} \quad (44)$$

$$\frac{C_6}{C_{20}} = \frac{\frac{K_4}{K_1} \frac{C_5}{C_{20}}}{\frac{\phi}{1-\phi}} + \frac{C_{60}}{C_{20}} \quad (45)$$

No allowance has been made for the effects of temperature and pressure in Eqs. (42) through (45). The reaction rate will vary with temperature as shown in Fig. 15, but product distribution will be nearly independent of temperature. McBee's data showed little or no effect of temperature on the relative reaction rates of the chlorination reactions. Pressure will not have a significant effect on the relative reaction rate. Neither should pressure affect the product distribution. In fact, results of actual commercial manufacturing operations show little or no effect on product distribution up to 100 lb/in.² gauge.

Equation (42), (43), (44), and (45) can be used to calculate a series of product distribution curves for a backmixed reactor corresponding to the

curves for a plug-type flow reactor. Such a set of product distribution curves for a backmixed reactor is shown in Fig. 17.

From the equations presented above, it is possible to predict the product distribution for any given methane conversion. The conversion can be related directly to an initial chlorine-to-methane ratio. Also, by using Fig. 15, the contact time required for any given conversion can be calculated. An interesting curve is shown in Fig. 18, which shows the time required for completion of a reaction in a plugflow reactor and a backmixed reactor. It will be noted that for a backmixed reactor, the reaction is never completed. However, in actual practice, a commercial reactor is a combination of backmixed and plugflow. Initially, the reaction is backmixed, but as the reaction products proceed down the reactor, the condition approaches plugflow and the reaction is completed. Some commercial reactors have had a special chamber attached to the end of the reactor system for effecting final completion of the reaction.

Should it be desired to recycle some of the lighter ends (methyl chloride or methylene chloride) to the reactor, the result of such a recycling procedure can be predicted. Figure 19 is a curve that shows product distribution resulting from recycling various amounts of methyl chloride to a mixed reactor at various ratios of chlorine to methane.

It should be pointed out that the above is based on theoretical considerations. In actual practice, other factors enter into the picture and affect the product distribution. Relative reaction rates have been calculated from three different commercial reactors and found to give different results. It is suggested that for a commercial reactor design, relative reaction rate data be determined experimentally from a pilot of the particular type of reactor to

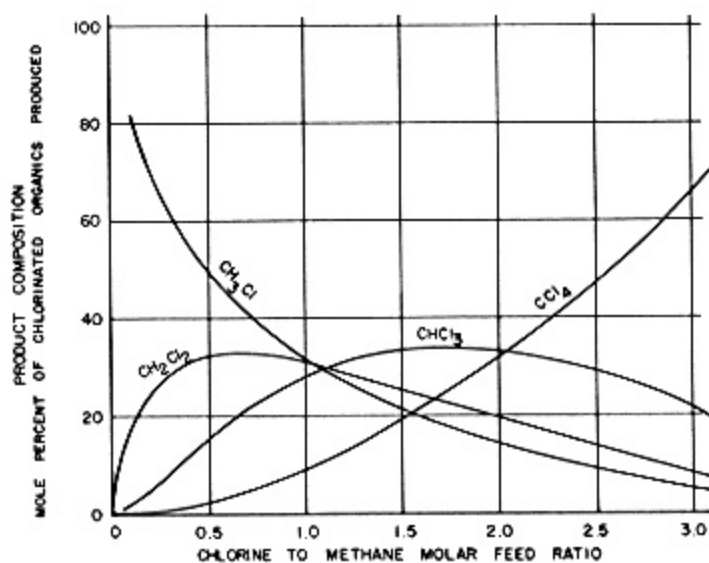


Fig. 17.
Methane chlorination product distribution from backmixed reactor
reaction rate constants from McBee data [18].

be used and this data used for the scaled-up reactor. Data determined in this manner and substituted in Eqs. (42), (43), (44), and (45) have been successfully used for the design of at least three known commercial chlorination reaction systems.

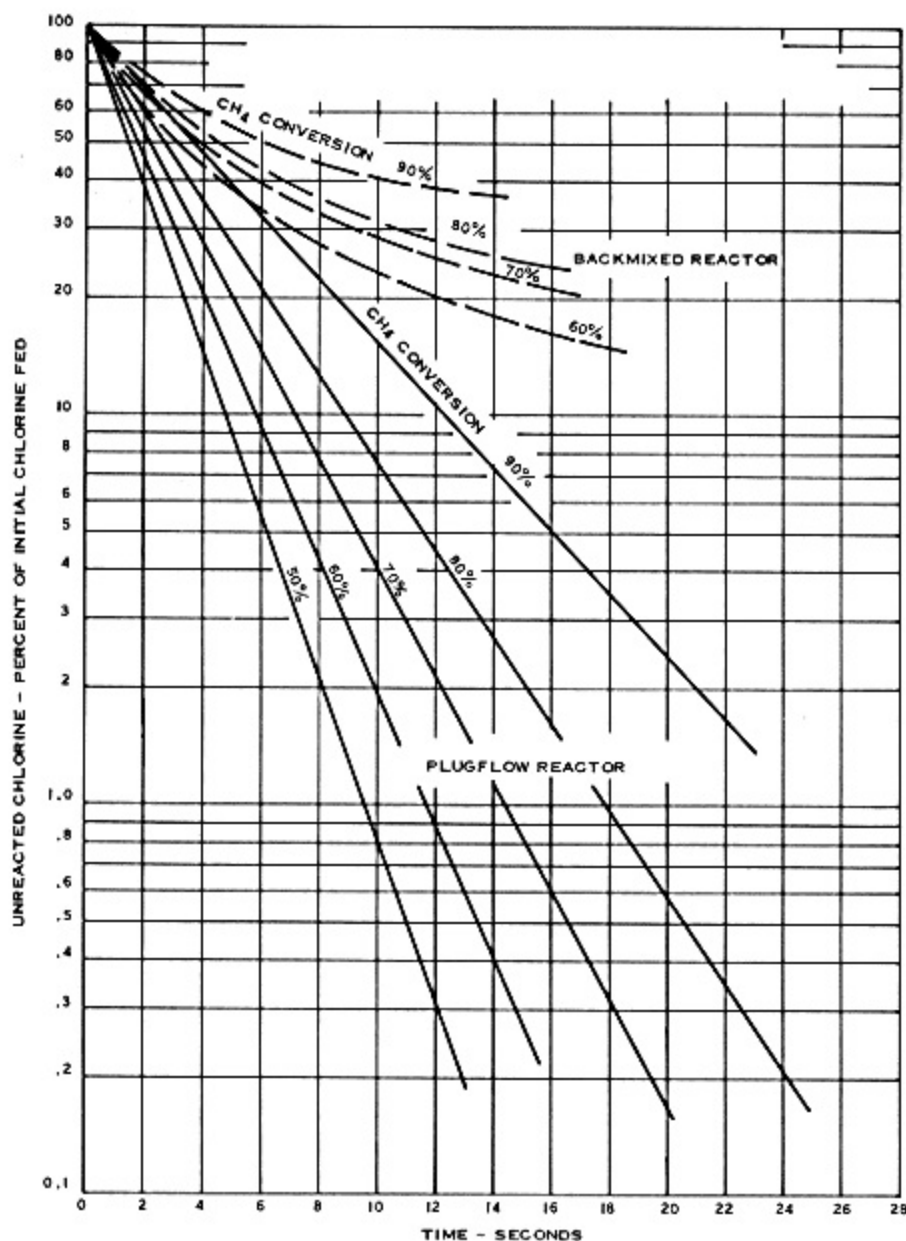


Fig. 18.

Thermal chlorination of methane chlorine conversions as a function of time for various ultimate methane conversions.

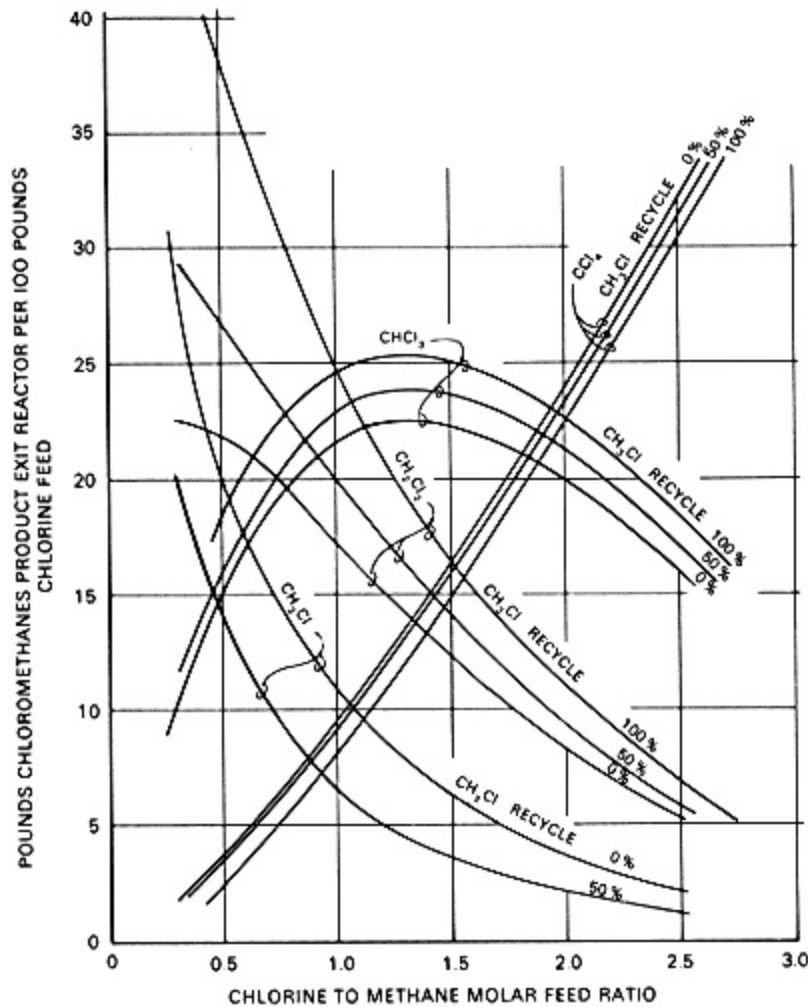


Fig. 19.

Product distribution for chlorination of methane in a backmixed reactor with various amounts of methyl chloride recycled. Figures on the curves are the percent of CH₃Cl leaving the reactor that is returned to the reaction zone.

Figure 20 shows actual data for chlorination of methyl chloride in a pilotplant reactor.

Commercial Plant Design for Chlorination of Methane

The design of the product recovery and purification section of a commercial methanes chlorination plant presents no serious problems. This is largely the application of good chemical engineering practices and the making of allowances for the physical characteristics of the components involved.

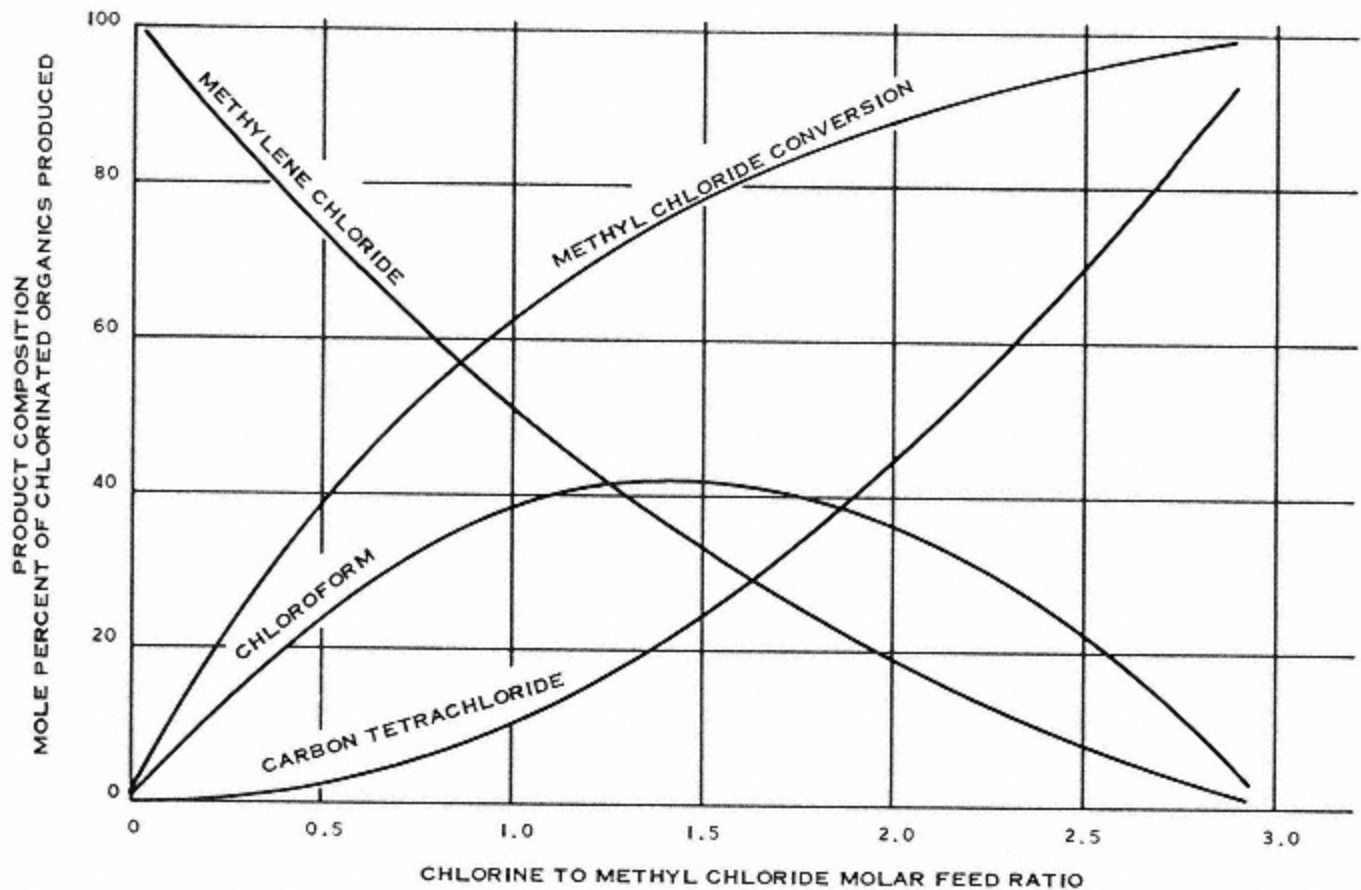


Fig. 20.
Thermochlorination of methyl chloride. Data from pilot plant.

However, the reactor section presents some problems not so easily solved. Reduction to commercial practice of the chemistry and kinetics of methane chlorination has occupied much effort over the years. There are several factors that make this reactor unit difficult to design. These can best be summarized as follows:

1. There is a high heat release relative to the heat-carrying capacity of the reacting gases. About 25,000 cal/g-mol (634.7 Btu/lb) of chlorine reacted is released by the reaction. The specific heat (heat-carrying capacity) of the gases involved is quite low relative to such a high heat release. The result is that at a ratio of methane to chlorine as low as 0.25 and relatively cool feed temperature, the resulting temperature of the reacting gases will be over 400°C for an adiabatic system. This ratio allows only a small fraction of the methane to be converted per pass through the reactor. This means some method must be employed for heat control if any sizable proportion of the methane must be employed for heat control if any sizable proportion of the methane is to be converted per pass.
2. A mix of methane and chlorine must be brought to over 300°C before the reaction can be initiated. This increases the heat control problem and lessens the conversion per pass unless a system can be designed to preheat the incoming gases with the reacting gases. This transfer must take place as the reaction is proceeding and not after the reaction has happened.

3. Temperatures much over 450°C cannot be tolerated or pyrolysis occurs. Pyrolysis is a very exothermic reaction and, once initiated, quickly reaches explosive violence with copious release of carbon.
4. Once initiated, the chlorination reaction goes very quickly with much of the heat release occurring within a fraction of a second. The speed of this

reaction is such that no mechanical means, such as normal heat transfer surfaces within the reactor, can be used for control of the heat of reaction.

5. Localized burning (pyrolysis) will occur from any momentarily high chlorine concentration occurring in the reactor such as during the mixing of a stream of vaporized chlorine into hot reacting gases. Pyrolysis results in carbon release in the reactor, which is a very troublesome problem.

Over the years a number of ideas have been tried to solve these problems in connection with the design of commercial methane chlorination units. A number of interesting different types of reactor designs have been proposed and a number of patents have been issued covering them [18, 2552].

Generally, all of the cited reference reactor systems operate without a catalyst, depending on temperature to activate the chlorine molecule. Basically, these reactor systems fall within the following general designs:

1. A sufficiently low ratio of chlorine to methane is fed to the reactor that the resulting temperature will be within acceptable limits. This requires considerable recycling of the methane and/or the resulting chloromethanes. Multiple reactors in series can be used rather than recycling to a primary reactor [53]. Reactors of this type may require preheating of the feeds. Reactor systems of this type are known to be in commercial use.
2. An inert diluent, such as nitrogen or HCl, is fed with the chlorine and methane. The diluent absorbs the heat of reaction and increases the permissible feed ratio of chlorine to methane. No known commercial reactors of this nature are now in use, probably due to the difficulty in condensing the organic products from the inert diluents.
3. Mechanical heat transfer surfaces within the reactor are used for the removal of the heat of reaction. This method has been tried without success, and there are no known commercial units.
4. The heat of reaction is absorbed by mixing carbon tetrachloride and/or lighter chloromethanes with methane and chlorine and feeding this mix to a reactor zone. The amount of diluent required is determined by the ratio of chlorine to methane in the feed to the reactor. The CCl₄ diluent is recovered by distillation and is recycled to the reactor. If properly designed, the feeds need not be preheated. This type of reactor system works well and is in commercial use in a number of chloromethanes plants.
5. A mixed feed of chlorine and methane is fed to a series of tubes submerged in a hot salt bath. The hot bath serves to bring the feeds up to reacting temperature and absorbs some heat of reaction. The bath cannot be depended upon to remove much of the reaction heat as it cannot be transferred nearly as fast as heat is released in the reactor. Carbon tetrachloride diluent and recycled partially chlorinated products can be fed with the reactants for further chlorination. It is not known if there are commercial units today of

this type, but they have been used.

6. There has been considerable interest in the use of fluid bed reactors for chlorination of methane. This would seem to be a good application of fluid beds if one could control the problem of recycling within the bed to prevent

overchlorination and shift of the product split disproportionately to chloroform and carbon tetrachloride. This should be a good reactor for production of carbon tetrachloride and perhaps chloroform. There may be some commercial operations in use today using a fluid bed reactor.

It is important for a methane chlorination unit to have high purity methane as feed to the reactor. All hydrocarbon content in the feed will chlorinate along with the methane and can cause difficulty in purification of the chloromethane products. It is much easier to purify the methane than try to remove products of chlorination of other hydrocarbons from the chloromethanes. Generally, the methane feed should not contain more than 100 ppm impurities, excluding nitrogen content. Some nitrogen can be tolerated, but it should be kept to a minimum as it will build within the recycled methane and require purging and loss of the purified methane. Carbon dioxide, oxygen, and any sulfur compounds must be removed from the methane. The method most in use today for preparation of a satisfactory feed methane is cryogenic distillation of natural gas or refinery fuel gases. This method of purification can easily produce a methane of 99.99% purity.

The method for recovery of condensables from the reactor effluent gases depends on the product distribution the plant is to produce. The degree of difficulty in recovery increases with increased emphasis on production of methyl chloride and methylene chloride. There are several ways this can be done. Generally, the methods fall into two basic approaches: (1) compression of the reactor effluent gases followed by condensation, and (2) refrigeration of the gases to low temperatures, without compression, for condensation of the chloromethanes products. Figures 21 and 22 show these two systems. The compression route is used where production of the lighter products is being emphasized and the refrigeration route where chloroform and carbon tetrachloride are being maximized. Generally, the HCl content of the reactor effluent stream is recovered by adsorption in water to make a muriatic acid product. This can be stripped for production of anhydrous hydrogen chloride to be fed to other chemical processes, or it can be sold as acid. Care must be taken in introducing water into the process stream that no carry-through occurs as this can cause serious corrosion in other parts of the plant. Also, the crude chloromethanes product sent to distillation for purification must not contain water or difficulty will be experienced with decomposition in the distillation train. Low compression ratios must be used for compressing chloromethanes containing gases as they are subject to decomposition and polymerization by high temperatures resulting from gas compression.

Purification of the chloromethanes consists of a distillation train with a column for each product. Dependent on characteristics of the reactor system used and purities of the feed chemicals, some additional purification processing may be required for final cleanup of the chloromethanes products to meet the exacting product purity now demanded by most users of these chemicals. Usually there are small amounts of ethane in the methane feed to the reactor. This ethane will be chlorinated and end up as contaminants in the

products. Also, since free radicals are involved in the reactor, some dimerizations will occur, resulting in C-2 and C-3 contaminants in the products. The reactor

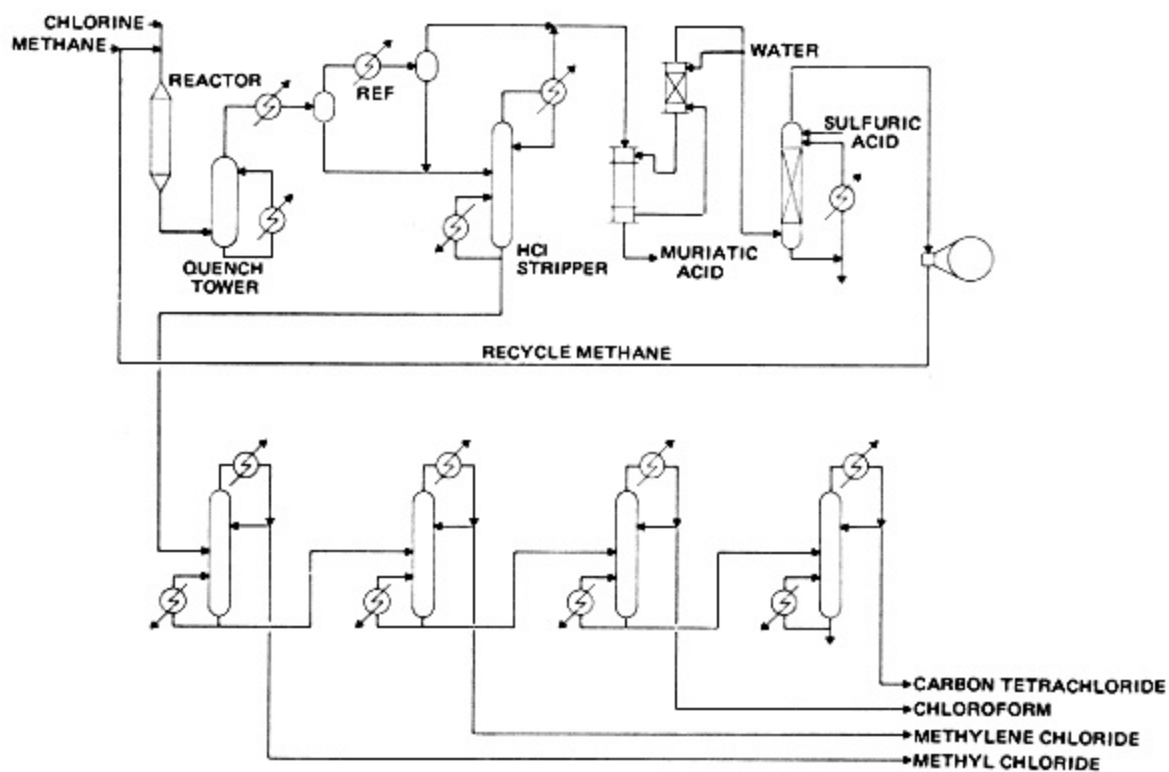


Fig. 22.

Chloromethanes by methane chlorination: product split favoring chloroform and carbon tetrachloride.

design will affect the degree of these side reactions. Some of the impurities thus derived are difficult to remove by distillation, so other processing methods must be used for their removal. This cleanup can be effected by such means as catalytic polymerization or dimerization, adsorption, or actinic light-induced chlorination of the contaminants to high boilers where they can be removed by distillation. These purification steps are usually inserted either between the distillation columns or in the final product stream coming from the product distillation column. Generally, it is desirable to keep polymers and heavy ends out of the distillation columns or problems can develop with frequent fouling of column reboilers. Also, it is important that temperatures in the bottom of the distillation columns be kept to a minimum to prevent decomposition and fouling of reboilers. For this reason there is a limit on the pressures that can be used in the distillation columns. Usually they are operated near atmospheric pressure.

A key to success in a chloromethanes plant is to keep all the process streams free of water. It is good practice to limit the water content of the circulating streams to less than 50 ppm of water. This minimizes corrosion where the streams contain hydrogen chloride or chlorine. Also, it helps prevent hydrolysis and decomposition of the chloromethanes in the processing steps. Metal chloride is always a problem in every plant. Accumulations will occur regardless of the care to prevent corrosion of metal parts in the plant. Care must be exercised to keep these out of the reactor feeds, column reboilers, and compressor suctions as they serve as a catalyst for product decomposition and promotion of side reactions.

Materials of construction consist of carbon steel, Monel, nickel, graphite, and plastic-lined pipe and vessels. Much of the plant, such as the distillation column and much of the connecting piping and tankage, can be made of a good grade of carbon steel. Nickel and Monel are used where elevated temperatures are encountered. Graphite and plastic-lined steel are used where water and hydrogen chloride are together in the processing equipment. Tetrafluoroethylene and polyvinylidene fluoride resins give the best service where plastics are used.

Yields for a typical methane chlorination plant will be about 95 to 96% of theoretical for chlorine. This yield includes all the chlorine recovered as HCl. The yield on methane will be about 90 to 92%, depending on the inert content of the purified methane. As the methane is recycled, the inert content builds up, necessitating a purge from the system. Yield on the original gas stream from which the pure methane is extracted will vary depending on the original methane content. Generally, it is not economical to try to recover more than 90% of the original methane as a pure feed product to the chlorination unit. The methane not recovered and the other hydrocarbons can usually be fed to a fuel system.

Photochlorination

Methane and its partially chlorinated derivatives can be chlorinated by activation of the

reaction mass with actinic light. Early in the history of

methane chlorination, 1940-1950, some commercial operations were based on this method of operation; however, in recent years this procedure has largely been replaced with the thermal method. Nevertheless, the photochlorination method has some virtues and should be included in any discussion of chloromethanes manufacture. While today it is not the primary method of chloromethanes production, there are reasons to believe it is used for cleanup and purification purposes in some processes. There are a number of good references in the literature to photochemical chlorination [5462].

The disassociation of the chlorine molecule to monatomic chlorine radicals is accomplished by radiating the reaction mass with a light source which produces radiation in the range of 3000 to 5000 Å. If the temperature is controlled so that thermal disassociation does not take over, the reaction is rather mild and good control is possible. The reaction medium can be either liquid or gas phase. The liquid phase perhaps offers the easiest means for temperature control, but it has the disadvantage of lower utilization of the light energy input. The liquids must be kept water white and totally free of any carbon or coloration by contamination with metal chlorides as these will serve to absorb the light and keep it from penetrating into the liquid. An ideal liquid system would be free of any gas bubbles as these tend to concentrate chlorine at the interfaces and result in overchlorination beyond that normally expected from the hydrocarbon-to-chlorine ratio fed to the reactor. Carbon can be formed and will cause coloration problems in the liquid chlorination media. Photochlorination is particularly good for removal of trace impurities of the lighter chloromethanes from carbon tetrachloride.

Vapor-phase photochlorination allows better utilization of the light input and allows better control of chlorine concentration than does liquid phase. It therefore offers the better opportunity for selectivity of product distribution in the reactor effluent. It has the disadvantage of being more difficult for heat removal and temperature control. This can be accomplished by recycle of carbon tetrachloride or other products of the reaction [65, 66]. Control of temperature and chlorine concentrations are important to prevent formation of any carbon in the reactor or else the lamps will become coated with carbon and the effectiveness of light input impaired.

Photochlorination seems to offer possibilities for speciality chlorinations, but it is doubtful if it is a good method for the primary reactor in chloromethanes manufacturing. In comparison with the thermal chlorination procedure, photochlorination seems to have the following disadvantages:

1. Requires energy input by way of photo lamps where the thermal process can utilize the heat of reacting of the chlorination to initiate the reaction and carry it to completion.
2. Photochlorination is carried out at a lower temperature which increases the cost for control and containment of the heat of reaction.
3. Much more sensitive to impurities in the feed chemicals, causing termination of the chain reaction.

4. Mechanical problem of light transmission to the reactions. Dirt or carbon on the surfaces of lamps or containing glasses and any coloration in the liquids absorb and waste the light energy.

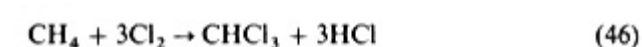
5. Material of construction problems. Lights and containers must be made of glass, which is costly and has high maintenance costs.
6. Low capacity per reactor.
7. Difficult to effect complete utilization of the chlorine in one pass through the reactor. This can result in an accumulation of chlorine downstream of the reactor and a subsequent explosion.

Catalytic Chlorination of Methane

There are a number of references in the literature [52, 6778] to the use of catalysts for the chlorination of methane. Much of this work was done in the earlier years of research on methods of chlorinating methane and, as the art has progressed, it has become more apparent that activation of the chlorine by high temperature offers advantages over catalytical methods. Some claims are made for catalysts which would favor the production of one chloromethane over another. However, it is doubtful if any catalyst is truly effective in the selective chlorination of methane. Except for oxychlorination, which is discussed later, there appears to have been little or no work done in recent years on the use of catalysts for promotion of the reaction between chlorine and methane.

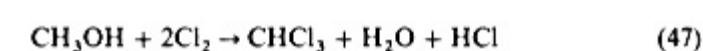
By-product HCl

When methane is chlorinated, one-half the total chlorine feed goes to by-product hydrogen chloride:



This conversion of chlorine to HCl can be a serious problem unless the plant is located near a market returning chlorine values for muriatic acid. One solution to this problem has been the use of muriatic acid for oil-well acidization, but this necessitates the chlorination plant being located near an oil-producing area. Another tonnage use for muriatic acid has been pickling of steel, but again, the plant has to be properly located. With development of technology for the oxychlorination of HCl to 1,2-dichloroethane, the problem of economical disposal of by-product HCl has been reduced. Today, large amounts of by-product HCl are used for oxychlorination of ethylenen to 1,2-dichloroethane and thence to vinyl chloride production.

Hydrochlorination of methanol results in less chlorine going to by-product HCl:



If methylene chloride should be the principal product, then theoretically no by-product HCl results because the single molecule of HCl coming from the thermal chlorination of methyl chloride is recycled back to hydrochlorination to produce methyl chloride. Actually, some excess HCl results because of

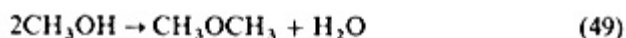
unavoidable polysubstitutions in the thermal chlorination step. Usually the yield is about 80% methylene, 15% chloroform, and 5% carbon tetrachloride. The extra HCl can readily be converted incrementally to methyl chloride and sold as this product, thus avoiding an HCl disposal problem. If greater quantities of chloroform are desired, and sales for methyl chloride are not available, then a home must be found for some HCl; but this is not nearly so great a problem as with methane chlorination. If the HCl is to be used for oxychlorination, it is fortunate that anhydrous HCl is more easily produced from a methanol hydrochlorination plant than from a methane chlorination unit.

Manufacture of Methyl Chloride by Hydrochlorination

Probably more methyl chloride is manufactured by the hydrochlorination of methanol than by any other method. Methanol will react with hydrogen chloride under mild dehydration conditions to produce methyl chloride. The hydroxyl group of methanol is replaced by chlorine from the hydrogen chloride molecule, and the result is methyl chloride and water:



A catalyst is required to promote this reaction to an acceptable rate and yield. An advantage of the process is that high yields are possible, and the single product methyl chloride can be produced with relatively little coproducts. Care must be taken that the reacting conditions do not favor the competing reaction whereby two molecules of methanol combine to produce dimethyl ether:



This is the only significant side reaction which takes place in the hydrochlorination reaction. Yields of about 94% of theoretical for methanol and 95% for chlorine are experienced in commercial operations.

At first look one might reach the conclusion that the use of methanol rather than methane as a source as a source of carbon for the production of methyl chloride would result in a more expensive operation. However, where only methyl chloride is desired and the plant capacity is relatively small, the hydrochlorination route offers some advantages over chlorination of methane. While the initial cost of the carbon from methane is less than from methanol, the actual difference in cost for raw materials for a methane chlorination unit and a hydrochlorination unit will amount to only a few hundred thousand dollars per year. This is a relatively small portion of the total yearly costs of the plant. The chlorine values and operating costs far overshadow the cost of the carbon source. Methane chlorination requires a very high purity methane for feed. This generally must be prepared by cryogenic distillation of natural gas. This is a relatively high investment unit and its operation is not inexpensive. Where principally methyl chloride is desired, a methane chlorination unit must be operated at a very low conversion of methane per pass. With the high vapor

pressure of methyl chloride and the large volume of gases to be handled, recovery of methyl chloride from the reactor effluent gases is a difficult and expensive operation. The large volume of gases handled and recycled results in the need for large equipment for a methane chlorination unit. Some of this is negated if methyl chloride is to be recovered only as part of a methane chlorination unit where the higher boiling chloromethanes would also be principal products from the plant. Significant quantities of methyl chloride are always produced as part of such a situation.

Another consideration in favor of a hydrochlorination route to methyl chloride is the fact that there is no by-product hydrogen chloride. Unless a good value can be realized for the HCl, this alone can more than offset the difference between the costs of methane and methanol. In the manufacture of chloromethanes there is much to be said in favor of combining the hydrochlorination route along with a thermal chlorination unit. This is particularly true if methylene chloride and methyl chloride are to be the principal products from the plant. If methyl chloride is thermally chlorinated to methylene chloride, only one molecule of hydrogen chloride results and this is recycled to a hydrochlorination unit to produce the feed methyl chloride. This makes a balanced system with regard to chlorine and involves little or no excess of HCl. Should significant quantities of chloroform be desired in addition to methylene chloride, the second molecule of hydrogen chloride can be consumed to make extra methyl chloride which usually can be sold more advantageously than HCl. This results in a closed cycle for the chlorine input to the plant. Of course, some carbon tetrachloride will result when chlorination is carried far enough to produce significant quantities of chloroform. This will result in added amounts of HCl which may have to be disposed of as muriatic acid. Figure 23 is a simplified flow diagram for a hydrochlorination unit integrated with a thermal chlorination system for the manufacture of chloromethanes. This is an efficient process and is used for a number of commercial chemical manufacturing operations for chloromethanes, both in the United States and in other countries. Yields for this type plant will be 92 to 93% of theoretical for methanol and 93 to 94% for chlorine.

It should be pointed out that where significant quantities of carbon tetrachloride are desired, this process is probably not the one to use. In fact, it is quite doubtful if either the chlorination of methane or the hydrochlorination of methyl alcohol is the most economical route to carbon tetrachloride. This product can be more economically produced either by way of the carbon disulfide method or by the perchlorination reaction producing the coproduct perchloroethylene.

The hydrochlorination reaction can be carried out using either a liquid or a solid catalyst. The liquid-phase reactor system operates at about 130 to 150°C. The solid catalyst reactor system must operate at about 300 to 350°C for complete reaction. The solid catalyst system has the advantage of higher throughput per reactor investment than the liquid-phase catalyst system. The liquid-phase system generally is carried out by bubbling mixed gases of HCl and methanol through a pot containing the liquid catalyst. Because of

the short contact time, the capacity of a pot is somewhat limited. Both liquid-phase and solid-phase catalyst systems are used in the United States and other parts of the

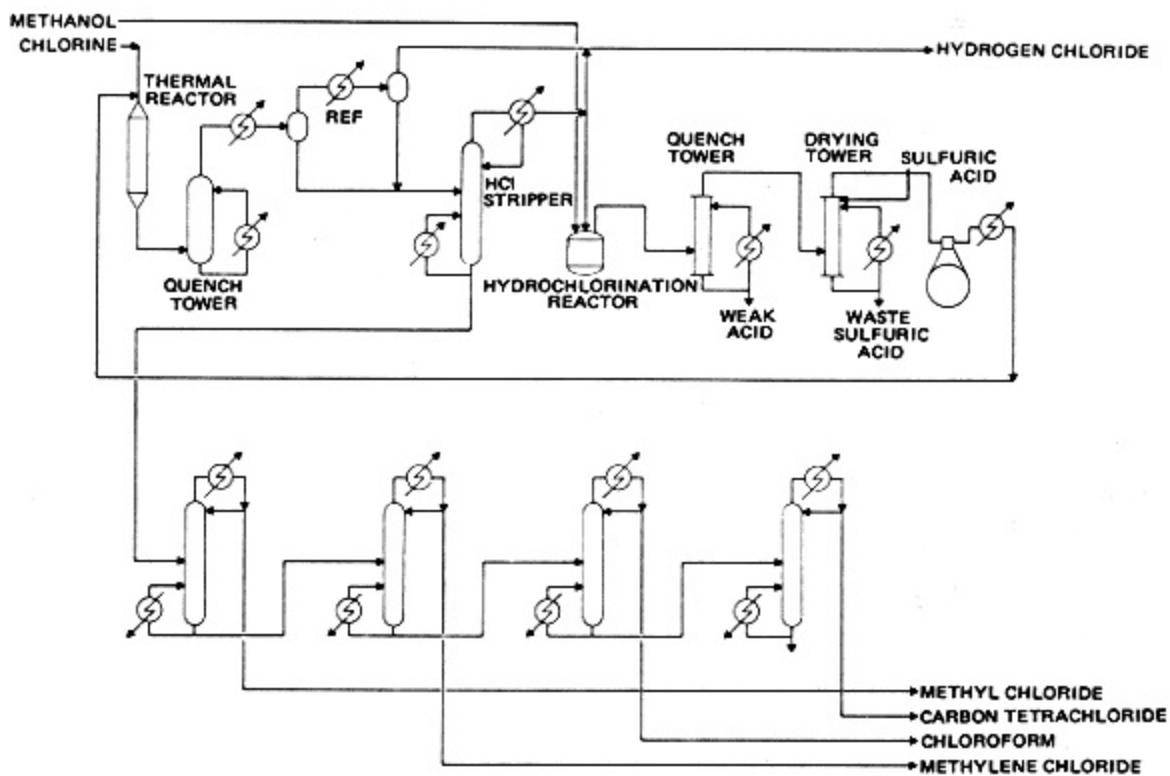


Fig. 23.
Chloromethanes manufacture from methyl alcohol.

industrial world. Except for the reactor, the process is very similar whether a solid-phase catalyst or a liquid-phase system is used.

Catalysts for the liquid-phase reaction are water solutions of metal chlorides such as ferric chloride and zinc chloride. The reaction is carried out by contacting the reacting gases with the water solution of the metal chlorides. The composition of the liquid catalyst is so adjusted that the temperature of the solution can readily be held at 140°C. The temperature must be sufficiently high to prevent condensation of water of reaction in the reactor; at the same time, it must not be so high that the reacting gases will sweep out catalyst solution water from the reactor. Stoichiometric feed ratios are used, and much of the HCl and methanol is converted in one pass. The unreacted methanol is recovered in the condenser and water scrubber downstream of the reactor. This is an acidic water solution and is difficult to handle, but it can be distilled for the recovery and recycling of the methanol content. The unreacted HCl is generally lost to water scrubbing and caustic neutralization of the reacting gases downstream of the reactor. Recovery of this HCl is quite difficult because the composition is on the water-rich side of the azeotropic between water and HCl, having a composition of only 20.2 wt.% HCl. Sulfuric acid is used to scrub the gases from the reactor both to remove the by-product dimethyl ether and dry the methyl chloride. Final recovery of the methyl chloride is effected by compressing the dried gas to about 110 lb/in.² gauge which forms liquid in a water-cooled heat exchanger.

The solid catalyst system is not unlike the vapor-phase system except for the reactor. Catalysts used include zinc chloride, copper chloride, and alumina; phosphoric acid has been suggested as a catalyst. The metal chlorides usually are deposited on a carrier such as carbon, silica gel, pumice, and alumina. Space velocities for the reactor are reported to be about 100 volumes of standard temperature and pressure gas per hour per volume of catalyst employed. It is believed actual commercial operations achieve yields up to 96% of theoretical based on methanol feed.

Table 5 shows a comparison of chloromethanes product distribution that can be expected from commercial manufacturing plants for both hydrochlorination of methanol and direct methane chlorination. More extreme product splits could theoretically be achieved, but these would not be practical from the viewpoint of plant capital costs and operating costs.

Manufacture of Carbon Tetrachloride by Way of Carbon Disulfide

Carbon tetrachloride has been made by way of carbon disulfide since 1893 and is still a major source of carbon tetrachloride in the United States. Perhaps as much as 40 to 50% of all carbon tetrachloride manufactured in the United States is by way of carbon disulfide. The only seriously competing method to carbon tetrachloride is the perchlorination of aliphatic hydrocarbons to produce carbon tetrachloride and perchloroethylene in combination. Circumstances would dictate which process is the most economical for a particular producer.

Manufacture of carbon tetrachloride from carbon disulfide results in no

TABLE 5 Chloromethanes Product Distribution Expected from Most Commercial Plants
Weight Percent of Total Organic Production

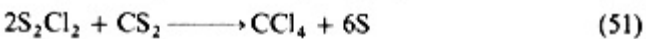
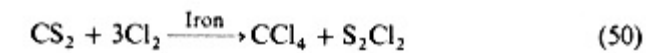
	Maximizing Methylene Chloride	Maximizing Chloroform	Maximizing Carbon Tetrachloride
Hydrochlorination methanola			
Methylene chloride	78		
Chloroform	19	80	5
Carbon tetrachloride	3	20	95
Percent methyl chloride converted per pass	22	40	58
Methane chlorinationb			
Methylene chloride	60		
Chloroform	33	75	10
Carbon tetrachloride	7	25	90
Percent methane converted per pass	15	18	25

aHydrochlorination of methanol followed by thermal chlorination of methyl chloride.

bDirect thermal chlorination of methane with 100% methyl chloride recycled.

coproducts of other chloromethanes, and no chlorine is downgraded to hydrogen chloride. Sulfur is a by-product of the process, which means the manufacturer of carbon tetrachloride by this method must also have a carbon disulfide manufacturing plant for conversion of the sulfur back to carbon disulfide. Generally, the carbon tetrachloride plant is an adjunct of the carbon disulfide plant. The carbon disulfide process can use chlorine cell gas from the chlorine manufacturing facility as feed chlorine to the plant. This is a factor which can favor the carbon disulfide process. Direct chlorination of hydrocarbons requires a liquefied pure chlorine as a feed. With the modern processes for production of carbon disulfide by catalytic reaction of methane with sulfur, the production of carbon tetrachloride by carbon disulfide is, in effect, a chlorination of methane. While indirect, in effect it uses methane as the source of carbon for the carbon tetrachloride without the attendant production of hydrogen chloride resulting from direct methane chlorination. The older plants were a bit messy, but newer, modern plants are as clean and neat as the direct methane chlorination units. It may be of some significance that there have been no new plants built in the United States in the last 20 years for the manufacture of carbon tetrachloride by way of carbon disulfide chlorination.

The chemistry for a carbon disulfide route to carbon tetrachloride is

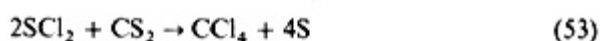


Reaction (50) takes place in the presence of iron as a catalyst. Reaction (51)

is a reversible reaction and means must be taken to drive it to completion. Generally, this is accomplished by an excess of carbon disulfide under several pounds of pressure [79, 80]. Sulfur from Reaction (51) must be recovered and recycled to a carbon disulfide plant. This can represent some problems in that the sulfur must be freed of chlorides before recycling. A possible variation in the handling of this sulfur would involve the chlorination portion of the sulfur which would be recycled back to the carbon disulfide reactor.

In early plants, Reactions (50) and (51) were carried out batchwise in large batch kettles. However, today most of the processes have been converted to continuous operations. A modern process now in use in Japan is presented by Fig. 24. Referring to the figure, the first reactor is charged with carbon tetrachloride. Chlorine is passed into the reactor which is maintained at about 30°C. Chlorination is used in excess to obtain a complete conversion of the carbon disulfide. The reaction product then contains a mixture of carbon tetrachloride and sulfur monochloride. This is passed to a still where a separation is made between carbon tetrachloride and sulfur monochloride. The carbon tetrachloride passes overhead while the sulfur monochloride goes to a second reactor where it is contacted with carbon disulfide to effect reaction as represented by Eq. (51) above. An excess of carbon disulfide is used in the secondary reactor to drive the reaction to completion. The resulting carbon tetrachloride and excess carbon disulfide are then recycled to the primary reactor. Sulfur from the secondary reactor must be processed for removal of the chlorides before it can be recycled to the carbon disulfide plant. Carbon tetrachloride from Still #1 will contain a certain amount of moisture and acidity. The acidity is neutralized in Vessel #2. Further treatment takes place in Vessel #3 by way of a bleaching liquid. Final purification of the carbon tetrachloride is effected in Still #2. This still must be capable of separating carbon tetrachloride from chloroform since a certain amount of chloroform is produced in the process as an impurity. The carbon tetrachloride is finally dried, either by way of calcium chloride in Vessel #4 or by an azeotropic distillation column. The product carbon tetrachloride will have a high purity if the processing has been done carefully; however, sulfur carried through from the process is one of the possible impurities.

A variation of the direct chlorination described above is possible by way of an indirect method represented by



In this process, sulfur is chlorinated to sulfur dichloride which in turn is reacted with carbon disulfide to produce carbon tetrachloride and sulfur. Sulfur equivalent to the incoming carbon disulfide is separated from the process and recycled to a carbon disulfide plant. This process is described in detail by Beanblossom and Scott patents [63, 64]. It is not believed this process is in commercial practice anyplace in the United States. However, variations of it may be in use outside the United States.

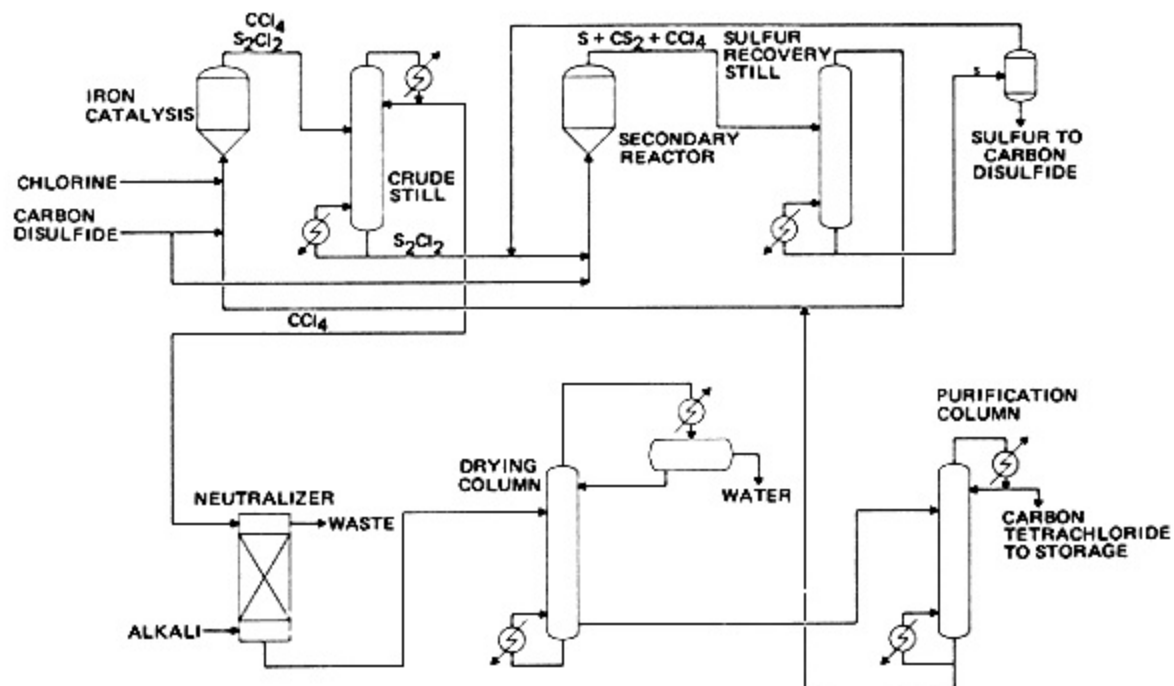
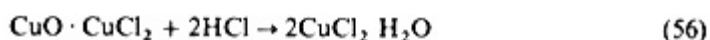
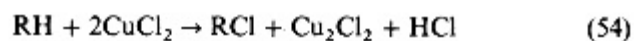


Fig. 24.
Manufacture of carbon tetrachloride from carbon disulfide.

Oxychlorination of Methane

There has been considerable interest and research work since the early 1960s on the oxychlorination of methane. This is a vapor-phase oxidative chlorination reaction in which air or oxygen and HCl are fed, along with methane, to a reactor which generally contains a copper chloride catalyst [8190]. The reaction is probably a combination of the old Deacon reaction and a molecular reaction between methane and cupric chloride. All four of the chloromethanes are produced, and selectivity is not too different from vaporphase chlorination, depending on the ratios of HCl and methane fed to the reactor. The reaction can be represented by



Overall:



Conceivably, chlorine rather than HCl can be fed to the reactor to effect a vapor-phase thermal chlorination. An oxychlorination reaction takes place simultaneously in the above manner to soak up HCl resulting from the thermal chlorination. The net result is methane chlorination without HCl production. Actually, in practice some unreacted HCl and/or Cl₂ comes through the reactor and appears in the exit gases. Much heat of reaction results and temperatures are difficult to control. A compromise temperature must be selected that is high enough to minimize the inhibiting effect of oxygen on the chain reactions of chlorine substitution and, at the same time, low enough to be favorable to the Deacon reaction. Temperatures at about 400°C seem to be the best. There is some indication that part of the reaction is nothing more than liberation of chlorine by the Deacon reaction followed by vapor-phase thermal chlorination of methane. This is borne out by the fact that in some experimental reactors free chlorine is found in the exit gases where only HCl was in the feed.

A number of catalysts have been reported [9193] and patents granted [9497]. Much of the work has been done in fluid beds to more easily control the high heat of reaction. Research work using fixed beds has been reported [98100], but generally fixed beds are not very satisfactory because of the heat removal problem. Most catalysts contain copper chloride as the active ingredient with KCl being added to stabilize the CuCl₂. The catalyst carrier is quite important for a successful catalyst; pumice, alumina, talc, and silica gel have been used as catalyst carriers.

Another approach to oxychlorination of methane is the use of fused salt melts [101107]. The feed gases are contacted with a molten salt. Copper chloride generally is the active ingredient of the catalyst with KCl and other metal salts added to reduce the melting

point of the mix. Reaction is conducted at 300 to 400°C. The method offers an effective method for control of the

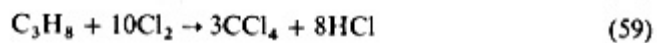
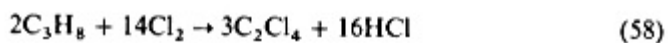
exothermic heat of reaction. However, the corrosive nature of the molten salt presents some difficult engineering problems.

To date, oxychlorination of methane has not been as successful as the oxychlorination of ethylene to make 1,2-dichloroethane. This latter process has been reduced to practice and many plants have been built. It is not believed a single commercial unit is in operation to produce chloromethanes by oxychlorination. One large plant utilizing fluid bed catalyst was announced in the late 1960s but later was canceled, supposedly due to economic reasons. A salt melt unit was announced for construction in Japan in 1974, but this unit has not been brought into production.

One of the difficulties with the oxychlorination of methane is that the competing reaction to oxidize methane and the chloromethanes to CO₂ is difficult to suppress. Reported yields to chloromethanes based on HCl feed generally run about 80 to 90% and on methane usually do not exceed 70% of theoretical. A high-purity methane is as necessary for feed as for the noncatalytic vapor-phase thermal chlorination process. The method offers some definite economic incentive if high enough yields can be obtained. Low-value by-product HCl from other sources can be used as the feed, and if chlorine is fed to the reactor, little or no by-product HCl is produced.

Carbon Tetrachloride by Perchlorination

Large amounts of carbon tetrachloride are commercially manufactured by the perchlorination of hydrocarbons containing two and three carbon atoms and their partially chlorinated derivatives. In contrast to the chlorination of methane, which operates with an excess of hydrocarbon, this reaction takes place in the presence of an excess of chlorine. This excess chlorine helps control the temperature of the exothermic heat of reaction and produces a coproduct of tetrachloroethylene (perchloroethylene):



The chlorination reaction takes place in the vapor phase at about 600°C. At this temperature, and in the presence of an excess of chlorine, an equilibrium condition exists between carbon tetrachloride and perchloroethylene:



The product distribution between carbon tetrachloride and tetrachloroethylene can therefore be controlled within certain limits by recycling the product least desired to the reaction zone. Selectivity of the predominant product varies with the feed hydrocarbon. When feeding propane and propylene, a selectivity as high as 90% of either product can be realized [108, 109].

There are side reactions in this perchlorination process which produce hexachloroethane,

hexachlorobenzene, and hexachlorobutadiene. The net production of hexachloroethane can be suppressed by recycling this compound

to the reaction zone. The other hex's cannot be reformed. Details of this process are discussed elsewhere in this Encyclopedia, and therefore no further details will be given in this section. However, it should be stated that the perchlorination process to make carbon tetrachloride has very favorable economics, particularly if some tetrachloroethylene is desired as a coproduct. If significant amounts of tetrachloroethylene are salable at normal market values, it is doubtful if methane chlorination, or perhaps the carbon disulfide route, can compete with this method for the manufacture of carbon tetrachloride. In some cases partially chlorinated compounds, which are normally waste products, are satisfactory as feed materials to the perchlorination process. For example, a number of perchlorination plants have been built as a means of upgrading wastes from vinyl chloride monomer to a salable product rather than incinerating them. This results in exceptionally attractive manufacturing costs of carbon tetrachloride and tetrachloroethylene.

Stability

With the exception of methyl chloride, the chloromethanes must be classified as being relatively unstable. They can be decomposed by high temperature, the action of oxygen from air, by hydrolysis with water, and by sunlight. A combination of moisture and air at elevated temperatures is particularly conducive to decomposition. This causes problems in commercial use of the chloromethanes and can cause considerable trouble in plants manufacturing chloromethanes. Proper materials of construction and operating conditions in manufacturing plants can prevent much of the stability problems. Stability of finished product methylene chloride and chloroform is controlled by the addition of stabilizers.

When speaking of the chloromethanes as being unstable, it is not intended to convey the idea that these chemicals are quantitatively converted to other compounds. In most cases only a relatively small portion deteriorates, but this is enough to cause difficulty in their use. For example, phosgene, a product of decomposition, is a very potent chemical and a very small content in methylene chloride would render it unfit as a paint stripper. A small content of HCl would make any of the chloromethanes very corrosive and unsuited for most uses.

The relative stability of chloromethanes to hydrolysis in order of least stability is

Chloroform

Carbon tetrachloride

Methylene chloride

Methyl chloride

The products of water hydrolysis of chloroform are formic acid and HCl. In the presence of small amounts of water, carbon tetrachloride will hydrolyze to

phosgene, chlorine, and hydrogen chloride. If sufficient water is available, the phosgene will also hydrolyze and the net result is CO₂ and HCl. Methylene chloride will form formaldehyde, HCl, and organic acids with water. Methyl chloride is relatively stable but will eventually hydrolyze to methanol and HCl. Hydrolysis is greatly speeded by high temperatures. Hydrolysis is catalyzed by the presence of metal salts such as ferric chloride.

Resistance to thermal decomposition of chloromethanes in order of most susceptibility is

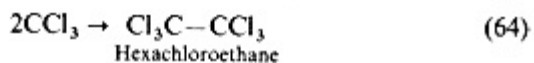
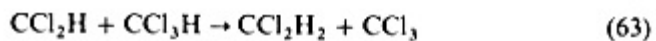
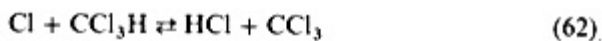
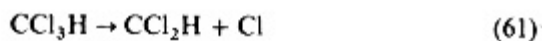
Carbon tetrachloride

Chloroform

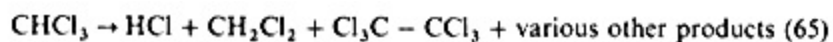
Methylene chloride

Methyl chloride

Thermal decomposition can occur in both the liquid and gas phase. Representative of thermal decomposition is [110]:



Net result



In the presence of steel and metal salts, such as ferric chloride, carbon tetrachloride will produce tars at temperatures as low as 150°C. Chloroform is somewhat more stable but cannot be expected to remain unaffected at temperatures much above 170°C. Again, the presence of iron and metal salts catalyzes the decomposition. Methylene chloride and methyl chloride are more thermally stable and can withstand higher temperatures. However, even these compounds will tend to carbonize and form black solid polymers in the vapor phase in the presence of steel and metal chlorides at 300 to 450°C. Carbon tetrachloride and chloroform vapors are much more susceptible to breakdown at elevated temperatures. This thermal instability results in the necessity for special considerations in manufacturing technology. The "know-how" to cope with these problems is extremely important in the design of chloromethane manufacturing plants. Generally, nickel and Monel are used at critical points of processing plants to control thermal decomposition.

Oxidative reactions will cause decomposition of chloroform; organic acids, HCl and phosgene are formed. Without a stabilizer, chloroform can hardly be kept overnight and remain "sweet" when in contact with the atmosphere. Chloroform is also susceptible to decomposition in the sunlight even when stored under an inert atmosphere, probably due

to slight amounts of dissolved

water and oxygen. Surprisingly enough, carbon tetrachloride is rather resistant to this type of reaction. In the pure state, kept dry and out of the sunlight, it can be stored for long periods of time and remain within manufacturing specifications.

Commercial methylene chloride and chloroform almost always contain stabilizers to prevent their decomposition. For most uses, cyclohexane is a satisfactory inhibitor for methylene chloride. Thymol, hydroquinone, p-cresol, and low-boiling amines have also been used as inhibitors. Where methylene chloride is used for aerosols, propylene oxide generally is also added. Methylene chloride has recently been used for vapor degreasing of metals. This is a difficult service and requires a special inhibitor system. A satisfactory one contains propylene oxide, butylene oxide, cyclohexane, and N-methylmorpholine.

Inhibitors for chloroform include pentenes, amylenes, and ethanol. The pharmaceutical grade of chloroform usually contains about 1% ethanol as the effective inhibitor.

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Chlorobenzene and Dichlorobenzene

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and E. W. Smalley

Industrial chlorination of benzene is carried out in the liquid phase at moderate temperature with the aid of a catalyst to produce monochlorobenzene, the three isomeric dichlorobenzenes, and small amounts of the more highly chlorinated derivatives. Chlorobenzene and the o- and p-dichlorobenzenes are the principal products. The meta-isomer is produced only in minor quantities. The more highly chlorinated derivatives are not normally produced in significant quantities and have only very limited industrial applications.

Physical and Chemical Properties

Chlorobenzene

Chlorobenzene, C_6H_5Cl , is a colorless, mobile liquid with an almondlike odor. Some of its physical properties are given in Table 1. It is soluble in all proportions in ether, chloroform, alcohol, benzene, and carbon disulfide. It is insoluble in water. Chlorobenzene forms both binary and ternary azeotropic mixtures with water and a number of organic liquids [4].

The chlorine atom in chlorobenzene is unreactive at ordinary temperatures and pressures. Even boiling for several hours with alcoholic potassium hydroxide has no effect upon chlorobenzene. Hydrolysis, with the formation of phenol, takes place at 450 to 500°C in the presence of a catalyst or with alcoholic alkalis or water under pressure at high temperatures. Aniline may be prepared by reaction of chlorobenzene with concentrated ammonium hydroxide under pressure in the presence of a copper catalyst.

Of technical importance is the preparation of DDT by condensation of chlorobenzene with chloral in the presence of fuming sulfuric acid.

Chlorination of chlorobenzene in the presence of a variety of catalysts produces predominantly the o- and p-dichlorobenzene isomers [5].

TABLE 1 Physical Properties of Chlorobenzene

		Refs.
Molecular weight	112.56	
Melting point (°F)	-49.4	1
Boiling point (°F)	269.6	
Specific gravity	1.10620/4	1
Vapor density (air = 1)	3.9	2
Latent heat of vaporization (Btu/lb)	139.6	1
Specific heat (cal (15°)/g · °C, at 68°F)	0.309	1
Flash point, closed cup (°F)	84	2
Ignition temperature (°F)	1184	2
Flammable limits, in air (vol.%, ntp)	1.3 (lower)	2
	7.1 (upper)	2
Vapor pressure (mmHg), Antoine equation constants	32108°F 108446°F	1
A	7.10690 6.94504	
B	1500.0 1413.12	
C	224.0 216.0	

o-Dichlorobenzene

o-Dichlorobenzene, C₆H₄Cl₂, is a colorless, mobile liquid having an aromatic odor. Physical properties are given in Table 2. o-Dichlorobenzene is soluble in alcohol, benzene, ether, and a variety of organic solvents. It is insoluble in water. It forms a number of binary azeotropes [4].

TABLE 2 Physical Properties of o-Dichlorobenzene

		Refs.
Molecular weight	147.01	
Melting point (°F)	1.0	1
Boiling point (°F)	356.7	1
Specific gravity	1.30620/4	1
Vapor density (air = 1)	5.1	2
Latent heat of fusion (Btu/lb)	37.84	3
Specific heat (cal (15°)/g · °C, at -55°F)	0.185	1
	32°F	0.270
Flash point, closed cup (°F)	151	2
Ignition temperature (°F)	1198	2
Flammable limits, in air (vol.% ntp)	2.2 (lower)	2
	9.2 (upper)	2
Vapor pressure (mmHg), Antoine equation constants		1
A	6.92400	
B	1538.3	
C	200	

TABLE 3 Physical Properties of p-Dichlorobenzene

		Refs.
Molecular weight	147.01	
Melting point (°F)	127.6	1
Boiling point (°F)	345.9	1
Specific gravity	1.45821°	1
Vapor density (air = 1)	5.1	2
Latent heat of fusion (Btu/lb)	53.4	3
Specific heat (cal (15°)/g · °C, at -58°F)	0.219	1
	127210°F	0.298
Flash point, closed cup (°F)	150	2
Vapor pressure (mmHg), Antoine equation constants		1
A	6.89797	
B	1507.3	
C	201	

The first stage in the chlorination of o-dichlorobenzene gives 1,2,4-trichlorobenzene as the principle product. Nitration of o-dichlorobenzene with strong nitric acid or fuming nitric acid yields principally 3,4-dichloro-1-nitrobenzene or 4,5-dichloro-1,2-dintrobenzene, respectively. The chlorine atoms in o-dichlorobenzene are relatively inert under moderate reaction conditions. Alkaline hydrolysis at about 200°C in the presence of a copper salt is required to produce o-chlorophenol, and o-chloroaniline is produced at 200°C with alcoholic ammonia.

p-Dichlorobenzene

p-Dichlorobenzene is a white, crystalline solid with a camphorlike odor. The crystals sublime at ordinary temperatures. Physical properties are listed in Table 3. p-Dichlorobenzene is soluble in most organic solvents but is insoluble in water. It forms a number of azeotropic mixtures [4].

Chlorination of p-dichlorobenzene yields principally 1,2,4-trichlorobenzene. It may also be nitrated or sulfonated but the products are of little technical importance.

Uses and Markets

Tables 4, 5, and 6 show the change in end use patterns for chlorobenzene and dichlorobenzenes in the United States over the past several years [68].

The use of chlorobenzene in the production of phenol has declined drastically since most phenol producers have changed to the cumene route.

TABLE 4 Chlorobenzene End Use (United States) [6]

	1969	1972	1974
Phenol (%)	51	40	10
DDT (%)	20	10	6
Chloronitrobenzenes (%)	24	32	50
Solvent and other (%)	5	18	34

TABLE 5 o-Dichlorobenzene End Use (United States) [7]

	1968	1971	1974
Chemical intermediates (%)	40	46	53
TDI solvent (%)	15	18	20
Dyes (solvent and intermediates) (%)	10	8	8
General solvent use (%)	30	24	15
Other (%)	5	4	4

Restrictions on the use of DDT in the United States have greatly reduced the demand for chlorobenzene for DDT production. There has been an increasing demand for chlorobenzene in dye manufacturing (chloronitrobenzene) and as a solvent. Demand for chlorobenzene has declined from 457.6 million pounds in 1971 to 365 million pounds in 1974. Chlorobenzene producers will stress production of dichlorobenzenes, and future growth for chlorobenzene will depend upon growth of dye intermediates and solvent uses.

There has been an increasing demand for o-dichlorobenzene for use as an intermediate, chiefly in pesticide manufacture. There has also been an increased demand as a solvent in tolylene diisocyanate production, although other solvents have been introduced in this market. Demand for o-dichlorobenzene in dyes production both as a solvent and as an intermediate has been relatively stable while its use as a general solvent has decreased. Demand in 1970 for o-dichlorobenzene was 75 million pounds and increased to 85 million pounds in 1974. Future demand will depend upon its growth as a chemical intermediate and in TDI production.

Ninety percent of the p-dichlorobenzene demand is in space deodorant and moth control. These are mature markets and future growth will probably

TABLE 6 p-Dichlorobenzene End Use (United States) [8]

	1967	1970	1973
Space deodorant (%)	35	30	50
Moth control (%)	55	60	40
Chemical intermediate and other (%)	10	10	10

follow the growth in gross national product. Demand in 1973 was 73 million pounds.

Prices and Price Patterns

The historical price pattern (19521973) for chlorobenzene has ranged from a low of 7.5¢/lb to a high of 10.25¢/lb for tank cars, works [6]. Because of rapidly rising raw material and energy costs, the current price is in the range of 28 to 30.5¢/lb, same basis. However, the bulk of chlorobenzene produced is consumed captively.

The price of o-dichlorobenzene during 19521973 has ranged from a low of 9.75¢/lb to a high of 16.5¢/lb for technical grade in tank cars, freight allowed [7]. Current price on the same basis is 2033¢/lb.

p-Dichlorobenzene prices for 1962 to 1972 have ranged from a low of 11¢/lb to a high of 16.5¢/lb in 200-lb drums [8]. Current price in 300-lb drums is 26.5¢/lb.

Producers

Table 7 lists the producers of chlorobenzene and dichlorobenzenes with their estimated capacities for 1974. In addition, there are two processors who

TABLE 7 United States Chlorobenzenes Producers: Estimated Capacities. (millions of pounds) [68]

Producer and Location	Mono	ortho	para
Allied Chemical, Syracuse, New York	16	8	8
Dow Chemical, Midland, Michigan	300	22	16
Monsanto Corp., Sauget, Illinois	115	16	12
Montrose Chemical of California, Henderson, Nevada	70		
PPG, New Martinsville, West Virginia	70	15	20
Solvent Chemical, Niagara Falls, New York		10	10
Dover, Ohio		3	4
Standard Chlorine, Delaware City, Delaware	75	48	60
Total	646	122	130
Chemical Products,a Cartersville, Georgia		2	3
Specialty Organics,a Irwindale, California		1	2
Total		3	5

aProcessor.

purchase mixtures of dichlorobenzenes and separate the isomers. Producers usually report the maximum capacity for each product even though all three products cannot be produced at maximum capacity at the same time. Therefore, estimates of capacity versus consumption based upon published capacity data can be misleading.

Dow Chemical Company is the largest single producer of chlorobenzene in the United States but consumes most of it captively to produce phenol. Dow has announced [9] that it will phase out phenol production from chlorobenzene and will replace and expand its facilities for producing more highly chlorinated products.

Most other chlorobenzene producers consume the bulk of their production captively. For example, Montrose Chemical converts its chlorobenzene to DDT production for export [6].

Producers tend to emphasize dichlorobenzene production or more highly chlorinated derivatives but usually have the capability to produce whichever derivative is in demand.

Theory of Liquid-Phase Chlorination of Benzene and Chlorinated Benzenes

There have been a number of papers published on the effects of temperature and various catalysts on the liquid-phase chlorination of benzene and chlorinated benzenes in both batchwise and continuous processes [5, 1517]. The experimental results have been interpreted in terms of reaction kinetics.

The liquid-phase chlorination of benzene and chlorinated benzenes in the presence of a catalyst is a consecutive, competitive reaction. Starting with benzene, chlorination produces monochlorobenzene which reacts further with chlorine to yield successively dichlorobenzenes, trichlorobenzenes, tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene. Theoretically, there are a total of 12 possible chlorinated benzenes, but under the reaction conditions used in industrial processes only a few of the possible products are formed in significant amounts. In particular, metadichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene are formed in nearly negligible amounts.

The chlorinated benzenes differ widely in reactivity toward chlorine in the presence of catalysts. They may be arranged in a series of decreasing reactivity: benzene > monochlorobenzene > o-dichlorobenzene > 1,2,3-trichlorobenzene > p-dichlorobenzene > 1,2,4-trichlorobenzene > 1,2,3,4-tetrachlorobenzene. It has been established that monochlorobenzene is so much more reactive than o-dichlorobenzene that chlorination through the dichloro-stage is almost complete before appreciable amounts of trichlorobenzene are formed. Likewise, 1,2,4-trichlorobenzene is so much more reactive than 1,2,3,4-tetrachlorobenzene that practically no pentachlorobenzene is formed before all the trichlorobenzene is reacted. Thus chlorination of benzene can be considered as taking place in three pairs of two stages each: (1) chlorination of

benzene to monochlorobenzene and dichlorobenzene, (2) chlorination of dichlorobenzenes to trichlorobenzenes and tetrachlorobenzenes, and (3) chlorination of tetrachlorobenzenes to pentachlorobenzene and hexachlorobenzene.

The effect of temperature on the rate of a chemical reaction is expressed by the Arrhenius equation:

$$k = Ae^{-E/RT}$$

where k is the specific rate constant

A is the frequency factor

E is the activation energy

R is the gas constant

T is the absolute temperature

If k' is the specific rate constant for the chlorination of benzene and k'' is the specific rate constant for the chlorination of monochlorobenzene, then k'/k'' is the relative rate constant K for the competitive chlorination of benzene and monochlorobenzene. K can be determined experimentally by the distribution of products, but both benzene and monochlorobenzene chlorinate too rapidly to allow the convenient determination of k' and k'' . Application of the Arrhenius equation to both reactions gives:

$$\log K - \log A'/A'' = \left(\frac{E'' - E'}{R} \right) \left(\frac{1}{T} \right)$$

where $K = k'/k''$ is the relative rate constant for the chlorination of benzene and monochlorobenzene, respectively

A'/A'' is the relative frequency factor

$E'' - E'$ is the difference in the activation energies of the two chlorination reactions

It can be shown by evaluating the experimental values of K at two different temperatures that the term $\log A'/A''$ is equal to zero within the limits of experimental error. The above equation then reduces to

$$\log K = \left(\frac{E'' - E'}{R} \right) \left(\frac{1}{T} \right) \quad (1)$$

Therefore, once the term $E'' - E'$ has been evaluated experimentally, K can be calculated at any temperature.

The solid line in Fig. 1 shows the variation in K as a function of temperature and is based on Eq. (1). The curve is based on unpublished results by Hanna [21] and is in good agreement with experimental values published by Bourion.

Hanna's results were obtained from batch chlorination experiments using mixtures of benzene and monochlorobenzene in the presence of ferric chloride and carbon disulfide.

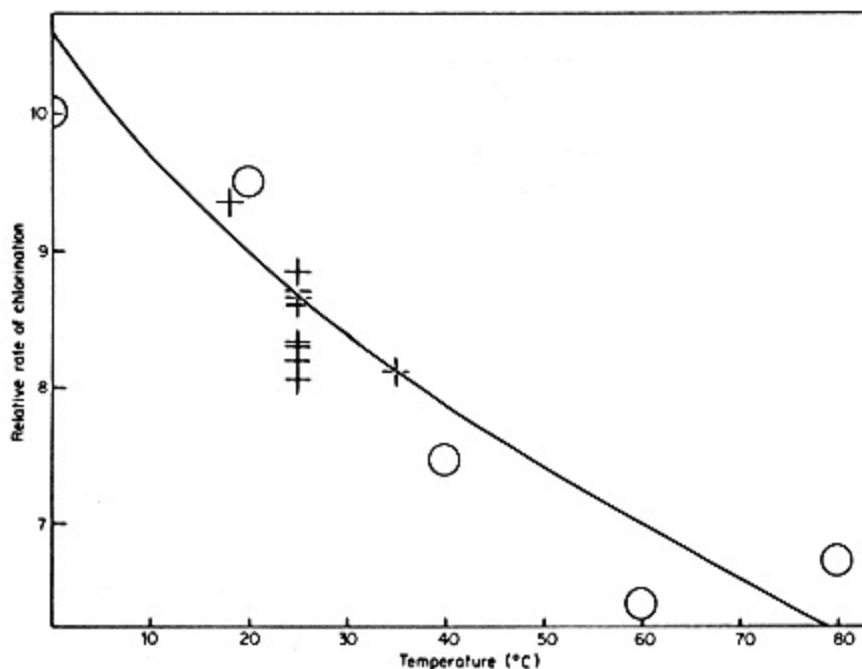


Fig. 1.

Variation of the relative rate of chlorination of benzene and monochlorobenzene with temperature. The open circles are laboratory data. The curve is from Bourion [15].

Equation (1) can be applied to the chlorination of other reactant pairs such as o-dichlorobenzene and p-dichlorobenzene, and p-dichlorobenzene and 1,2,4-trichlorobenzene, and curves similar to that of Fig. 1 can be obtained.

The Arrhenius equation can also be applied to the chlorination of monochlorobenzene to determine the effect of temperature on o- and p-dichlorobenzene isomer formation. It can be hypothesized that the reaction takes place in the following two steps:



In Reaction (2) a highly reactive intermediate is formed with the catalyst which can react further as in Reaction (3) to give either p- or o-dichlorobenzene plus HCl and free catalyst. Because of the ortho-para directing effect of the chlorine atom in monochlorobenzene, m-dichlorobenzene is formed in negligible amounts. Applying the Arrhenius equation to Reaction (3), let k' , A' , E' and k'' , A'' , E'' be the specific rate constant, frequency factor, and activation energy, respectively, for the intermediate reacting to form p-dichlorobenzene

and reacting to form orthodichlorobenzene:

$$\log K - \log A'/A'' = \left(\frac{E'' - E'}{R} \right) \left(\frac{1}{T} \right) \quad (4)$$

where $K = k'/k''$ is the relative rate constant for p- and o-isomer formation. The equation can be evaluated experimentally by determining K at two temperatures, and $\log A'/A''$ is found equal to $\log 1/2$ which is consistent with the fact that chlorine can react with monochlorobenzene in only one position to give the p-isomer or in two positions to give the o-isomer.

The solid line in Fig. 2 shows the variation in the yield of p-dichlorobenzene as a function of temperature and is based on Eq. (4). The experimental points are from the work of Hanna.

Starting with benzene alone, the concentrations of monochlorobenzene, dichlorobenzene, and unreacted benzene can be calculated from reaction kinetics for various degrees of chlorination when the appropriate relative rate constants are known. More highly chlorinated products are formed in negligible amounts under the conditions used in commercial practice. The following differential equations may be set up:

$$d\bar{A}/dt = k_1[\text{Cl}]A \quad (5)$$

$$d\bar{B}/dt = k_2[\text{Cl}]B \quad (6)$$

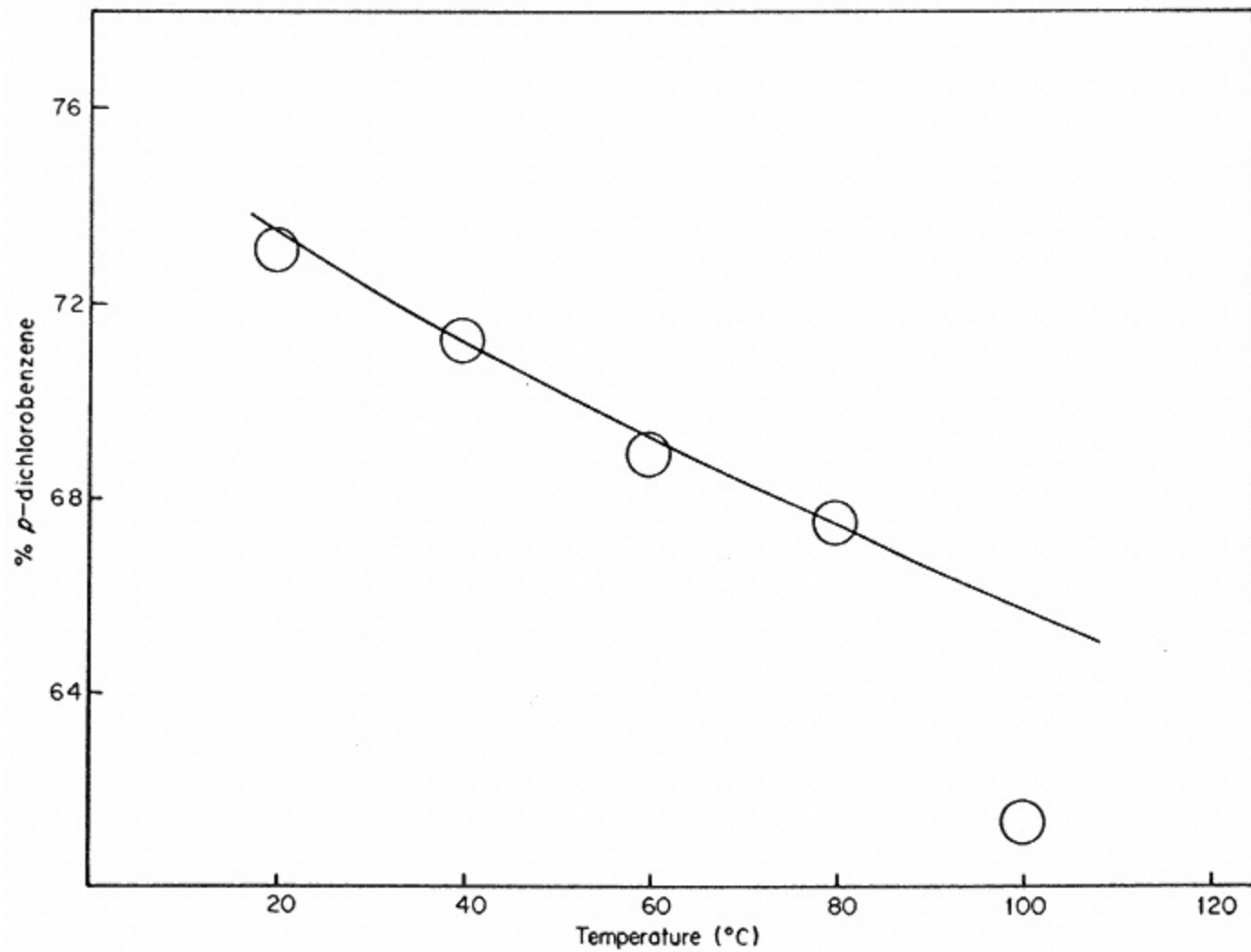


Fig. 2.
Variation of the yield of p-dichlorobenzene with temperature.

k_1 and k_2 are the specific rate constants for the wherechlorination of benzene and monochlorobenzene, respectively

\bar{A} and \bar{B} are the mole fractions of benzene and monochlorobenzene reacting with chlorine, respectively

A and B are benzene and monochlorobenzene present, respectively [Cl] is the chlorine concentration

Dividing Eq. (5) by Eq. (6) gives

$$\frac{d\bar{A}}{d\bar{B}} = \frac{k_1}{k_2} \frac{A}{B} \quad (7)$$

The following relationships are apparent:

$$A = A_0 - \bar{A} \quad (8)$$

$$B = B_0 + \bar{A} - \bar{B} \quad (9)$$

where A_0 and B_0 are the concentrations of benzene and monochlorobenzene originally present, respectively.

Differentiation of Eqs. (8) and (9) and substitution in Eq. (7) gives

$$\frac{dB}{dA} - \frac{K_1 B}{A} = -1 \quad (10)$$

where $K_1 = k_2/k_1$. Equation (10) is in the form of a first-order linear differential equation and may be solved by standard methods [22]. The solution of Eq. (10) is

$$B = \frac{-A}{1 - K_1} + \left(\frac{B_0}{A_0^{K_1}} + \frac{A_0^{1-K_1}}{1 - K_1} \right) A^{K_1} \quad (11)$$

In the special case starting with benzene alone, Eq. (11) reduces to

$$B = \frac{1}{1 - K_1} \left(A^{K_1} - A \right) \quad (12)$$

Neglecting more highly chlorinated products, the mole fraction of o- plus p-dichlorobenzene can be calculated by difference.

Figure 3, based on Eq. (12), shows the change in concentration of benzene, monochlorobenzene, and dichlorobenzenes as a function of the degree of chlorination assuming a relative rate constant of 8. Similar curves would be obtained at other relative

rate constant values.

The relative rate constant is a function of temperature only. Figures 1 and 3 can be used together to estimate the composition of the mixture obtained upon chlorinating benzene to a given degree at a given temperature. For example, if benzene is to be chlorinated at 40°C, the relative rate constant is about 8 (Fig. 1). If the total amount of chlorine added is equivalent to the total

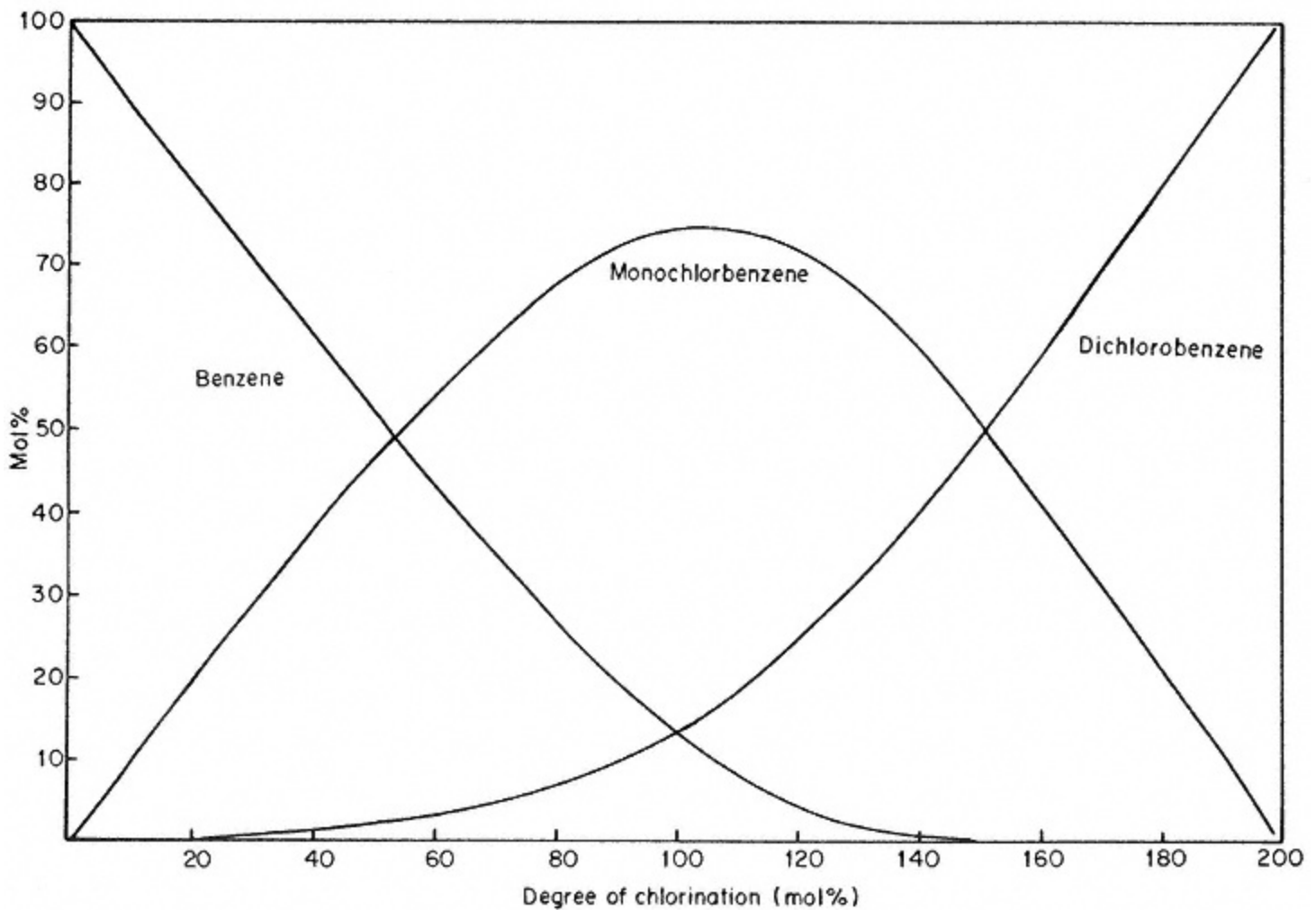


Fig. 3.

Chlorination of benzene with benzene chlorinating 8 times as fast as monochlorobenzene.

initial amount of benzene present (degree of chlorination is 100%), the resulting mixture will contain about 13 mol% benzene, 13 mol% dichlorobenzene (ortho plus para) and 75 mol% monochlorobenzene. In addition, from Fig. 2 the 13 mol% dichlorobenzenes formed will be about 71% p-isomer and 29% o-isomer.

MacMullin [17] has derived expressions for the relative rates of product formation in batch chlorination and for one- and two-stage continuous chlorination. His results indicate that the maximum amounts of mono-, di-, and trichlorobenzenes are obtained in batch chlorination for a given degree of chlorination. In addition, a system having an infinite number of stages with the liquid flowing from one reactor to the next and chlorine being introduced at each stage gives a product distribution identical to batch chlorination. However, a single-stage continuous reactor into which fresh benzene is flowing and chlorinated product is being removed will give the least selective product distribution, i.e., lower concentrations of mono- and dichlorobenzene relative to batch chlorination at the same degree of chlorination.

The relative amounts of o- and p-isomers in the dichlorobenzene fraction are affected by a number of process variables. Increasing the degree of chlorination beyond 2 mol of chlorine per mol of benzene results in increased p-isomer in the dichlorobenzene fraction

[5]. This is because the o-isomer chlorinates more rapidly than the p-isomer to trichlorobenzene. As Fig. 2 illustrates, with a particular catalyst chlorination at lower temperature favors formation of the p-isomer in the dichlorobenzene fraction.

The results of the affects of various catalysts on the o-p-isomer ratio in the dichlorobenzene fraction have been published in the technical and patent literature [5, 18, 19]. Ferric chloride and AlCl_3 have been widely used as substitutive chlorination catalysts and when used alone usually give a para-ortho ratio of about 1.4:1 in the dichlorobenzene fraction. Using either CS_2 or S as cocatalyst with FeCl_3 increases the para-ortho ratio to about 3:1. Other metal halides such as SbCl_5 , SnCl_4 , MoCl_5 , TiCl_4 , and mixtures of AlCl_3 - SnCl_4 and AlCl_3 - TiCl_4 have been evaluated as catalysts. Direct comparison of results are difficult because of the wide differences in experimental conditions, but para-ortho ratios of the order of 2:1 to 3:1 are usual. Few new data have been published in this area in recent years.

Purification of Chlorobenzenes

The area of separation and purification of chlorobenzenes has received the most attention in the last 20 years compared to other areas of chlorobenzene technology. The bulk of the published literature refers to continuous fractional crystallization apparatus and processes.

Brodie disclosed a solid-liquid continuous countercurrent purifier method and apparatus [10]: Figure 4 shows a schematic diagram of the apparatus taken from the patent. This is one of several arrangements of the elements of the apparatus.

There are three main sections; (1) a refining section, (2) a recovery section, and (3) a purifying section. Helical scraper-conveyors (4) and (5) are provided in the recovery and refining sections which slowly revolve, moving precipitated crystals toward the purifying section and liquid countercurrent to the crystals

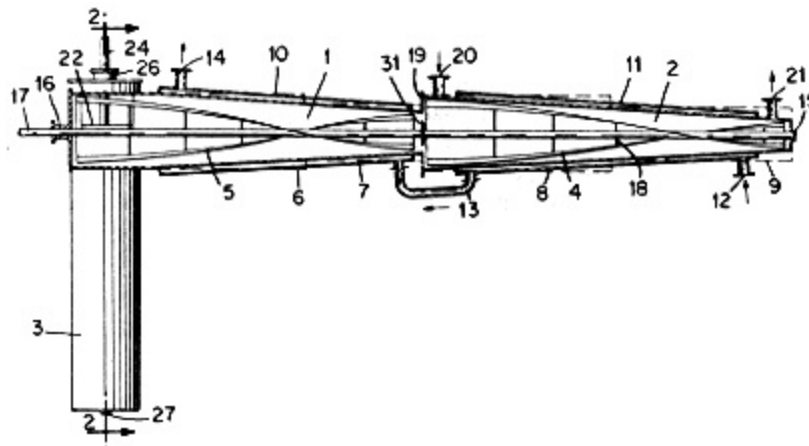


Fig. 4.
Solid-liquid continuous countercurrent purifier apparatus.

movement through the refining section and recovery section to the liquid outlet at (21). Coolant is introduced at (12) to the jacketed recovery (11) and refining (10) sections and exits at (14). A liquid feed enters at (20) in the recovery section just adjacent to the refining-recovery section junction at (19). The feed temperature should be just at the crystallizing point so as not to dissolve crystals already present nor to shock-cool the liquid phase which would cause excessive nucleation at the feed entry point. The crystals are lifted over weir (22) by the scraper-conveyor and fall by gravity through the purifying section (3). The purifying section has a slowly moving stirrer which gives an unagglomerated crystal bed. The crystals at the bottom of the bed are heated just sufficiently to cause melting, and a portion of the melt is withdrawn as pure product while the remainder passes upward, being displaced by the falling crystal bed. The rising liquid passes into the refining section.

Union Carbide Australia claims that a purity of 99.5 to 99.9% can be obtained consistently when using simple eutectic mixtures, with investment and operating costs 25 to 50% lower than with conventional crystallization systems.

Ramsay describes an apparatus for fractional crystallization [11]. The apparatus consists of a pair of metal tubes spirally wound on an inner casing, with an outer casing fitting over the metal tubes, resulting in an elongated helical vessel between the two casings. The helical vessel has an inlet at one end and an outlet at the opposite end with a feed inlet at the middle. The spirally wound tubes are used to alternately cool and heat the contents of the helical vessel. After cooling the contents of the helical vessel the liquid phase is displaced from one end of the helical vessel from the crystals formed during cooling. Part of the crystals is remelted by heating and the liquid displaced from the opposite end of the helical vessel. A purity gradient is therefore established along the length of the helical vessel. This cycle is repeated a number of times with fresh feed being introduced between cycles. An example is given for the purification of a mixture containing 95.8% p-DCB and o-DCB. After completing 11 cycles using 41°C water for cooling and heating at 60°C, the product contained 99.6% p-DCB.

Wiegandt [12] has patented a fractional crystallization process in which an immiscible liquid is cooled and introduced into the liquid mixture to be purified, causing crystallization of one component as droplets of the immiscible liquid pass through the liquid mixture. The crystals settle on a grid which can be heated to melt part of the crystals, and the melt passes over the settling crystals, thus increasing their purity. Depending on the density of the various phases, the melt is withdrawn at some point as liquid product. In the examples cited for the purification of dichlorobenzenes, aqueous solutions of $\text{Ca}(\text{NO}_3)_2$ were used as the immiscible liquid. Starting with a melt containing 93% p-DCB and cooling the aqueous solution to 25°C before spraying it into the dichlorobenzene melt, a bed of crystals was allowed to settle on a heated grid. The melt produced at the grid was passed upward through the crystals as they settled on the grid. After 1 h the melt produced at the grid had a crystallization temperature of 52.7°C (p-

DCB, 52.75°C). The top liquid contained 80% p-DCB and 20% o-DCB.

Procko [13] has patented a process for the purification of o-DCB by

reaction with 0.5 to 5% titanium tetrachloride at reflux temperatures. The reaction is specific for o-DCB. The contaminants removed are sulfur-containing organics such as thiophene and chlorinated thiophenes. Upon heating the o-DCB (70 to 95% purity plus p-DCB) with TiCl_4 at 183°C (reflux for 2 h), a black sludge forms which can be separated by decantation and then the o-DCB can be distilled. The reaction must be carried out under essentially anhydrous conditions to prevent hydrolysis of the titanium tetrachloride.

Poffenberger describes a freezing apparatus for producing solid p-DCB [14]. The apparatus produces a flat plate 4 ft by 12 ft and 1/2 in. thick. These plates are claimed to be an improvement over solid p-DCB produced in the "tube ice" machine (a device having vertical tubes in which solid is first frozen on the wall and then the tube is quickly heated to melt the layer of the solid which is next to the tube wall, thus permitting the tube of solid to slide out by gravity) in that fewer fines are produced during removal of the plate from the apparatus because the fracture line which is produced when using the "tube ice" machine is avoided. When operating the freezing apparatus during the cooling cycle, the initial coolant temperature is 30°C . After a flat plate has been formed the temperature of the coolant is reduced to 15°C with circulation continued for a "time."

Ratje was issued a patent for an apparatus for separation by crystallization [20]. The apparatus consists of a cylindrical purification chamber fitted with a piston which displaces a crystal mass downward toward the bottom of the chamber where heat is applied to melt a portion of the crystals, and the melt passes upward through the crystal mass, extracting impurities, and then passing from the chamber through a filter for recycle or further treatment. The product is withdrawn from the heated end of the purification chamber as a melt. The crystal mass is fed to the purification section through the side of the upper part of the purification section from a chamber which also contains a piston which displaces a crystalline mass into the purification section. The piston in the first chamber has a perforated face to remove liquor while it is compacting the crystalline mass, and the face of the piston is curved to conform to the contour of the purification section wall. The perforated curved face of the piston is claimed to allow uniform compacting of the crystal mass and provide a smooth uniform wall in the purification section, which reduces shearing of the crystals. An example cites the purification of a mixture of xylene isomers containing benzene and toluene. The feed contained 17% (wt.%) p-xylene and the product was about 99% p-xylene. It is not known if this type of apparatus has been applied to the purification of chlorobenzenes.

Manufacturing Process

United States production of chlorobenzene and dichlorobenzenes is based upon liquid-phase chlorination of benzene in the presence of a catalyst. At one time the large quantities of chlorobenzene used in phenol production were prepared by vapor-phase reaction of benzene, air, steam, and HCl over a

copper oxide catalyst, but the process is not economical except on a very large scale [23].

Figure 5 is a schematic diagram of one of several process schemes which can be used to manufacture chlorobenzene and/or dichlorobenzenes [24]. The process may be operated to produce principally chlorobenzene or to maximize production of o- and p-dichlorobenzene depending upon demand for a given product. The chlorination process may be operated batchwise or continuously.

Benzene used in the process should be free of paraffinic impurities and side-chain aromatics, and it should be thoroughly dried with solid caustic soda, silica gel, or by azeotropic distillation. Chlorine gas can be supplied as revaporized liquid or as compressed cell gas dried with concentrated sulfuric acid. If the chlorine utilized is cell gas, which contains hydrogen and oxygen, proper precautions should be taken to ensure that an explosive concentration of hydrogen does not occur in the vapor stream from the chlorinator nor in the downstream hydrogen chloride recovery system.

Since the reactants are dry, the chlorinator may be constructed of iron or steel in the form of a deep tank or horizontal vessel. Cooling is provided by internal coils or external circulation through a heat exchanger. Chlorine gas is sparged into the bottom of the chlorinator through a pipe. There may be several chlorinators operated in parallel or series depending upon the degree of chlorination of benzene desired.

Ferric chloride is usually used as catalyst. This can be added as a solution in benzene (0.1 parts FeCl_3 :100 parts total benzene) or as iron turnings or scrap (about 1% by weight of benzene) which provides ferric chloride in the chlorinator.

With respect to Fig. 5, the chlorinator is charged with benzene at start-up, and chlorine gas and fresh benzene are then added continuously at such a rate that chlorine breakthrough does not occur. The desired reaction temperature (about 40°C for chlorobenzene production and 55 to 60°C for dichlorobenzene) is maintained by circulation of the liquid through the external cooler. Fresh benzene may be added to the cooled circulated liquid. The degree of chlorination may be determined by density measurements, and the relative feed rate of chlorine and benzene adjusted accordingly. The chlorinated product is withdrawn continuously to the neutralizer.

The HCl gas coming from the chlorinator is contaminated with benzene and chlorinated products. The contaminants are removed by scrubbing the gas stream with refrigerated chlorobenzene. The spent chlorobenzene from the scrubber is sent to the neutralizer for further processing.

The HCl gas from the top of the scrubber next passes to a Korbate falling film absorber which is water cooled. Here the gas is absorbed in water or dilute HCl to produce commercial grade muriatic acid. It is possible to purchase "package" HCl recovery systems from a number of vendors. A "tails" tower where the last traces of HCl are

absorbed in water may be employed downstream before the remaining inert gas is vented to the atmosphere. Adsorption on activated carbon may be employed to remove any last traces of organics in order to comply with strict emission standards.

In the neutralizer, dissolved HCl is reacted with 10 to 25% caustic solution and maintained slightly alkaline in order to protect downstream equipment

from corrosion. Good contact between the caustic solution and organic phase is obtained by continuous circulation or agitation of the contents of the neutralizer. After neutralization the mixture is sent to a decanter where the aqueous and organic phases are separated. The aqueous phase may be further treated to remove organic contaminants before disposal.

The organic phase from the decanter is sent to a flash drum where benzene, chlorobenzene, and dichlorobenzenes are taken off overhead. The bottoms contain predominantly higher chlorinated products and tars. These bottoms may be further processed to recover higher chlorinated benzenes or incinerated.

The overhead from the flash drum goes to the benzene recovery column. This may be a conventional bubble cap fractionating column with 15 to 20 trays operated at atmospheric pressure. The benzene fraction taken off overhead typically contains about 98% benzene and 2% chlorobenzene and is recycled to benzene storage. The bottoms are predominantly chlorobenzene and dichlorobenzene which go to the chlorobenzene column.

The chlorobenzene column may contain 12 to 20 trays and is operated at 3 to 7 lb/in.² abs at 100 to 120°C. The chlorobenzene product is taken off overhead. The composition of the bottoms can be checked by specific gravity measurements. The column bottoms, containing o- and p-dichlorobenzene, are further processed, usually by fractional crystallization.

The scraped surface crystallizer shown in Fig. 5 is only one of several continuous fractional crystallization processes available. In this process the crystal slurry moves countercurrent to the jacketed cooling water. In the first stage of the fractional crystallization the mixture of dichlorobenzenes from the bottom of the monochlorobenzene column is cooled to about 40 to 45°C and the slurry is pumped to the scraped surface crystallizer where it is further cooled to about 35°C. The p-dichlorobenzene crystals are separated in a centrifuge and may be remelted and subjected to a second-stage recrystallization at lower temperatures in order to obtain p-dichlorobenzene of high purity. The recovered crystals are ground and classified into various mesh size. Fines can be remelted and recycled to the second-stage crystallizer. The mother liquors from both crystallizer stages, which are rich in o-dichlorobenzene, are combined and sent to a vacuum distillation column.

The vacuum column operates at about 6 to 10 lb/in.² abs and can give technical grade o-dichlorobenzene in the overhead take-off. The bottoms can be recycled to the process.

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Chlorolysis, Carbon Tetrachloride from Hydrocarbon Waste

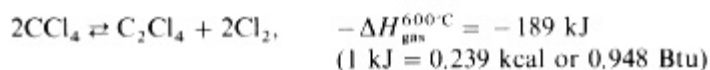
D. Rebhan

Chemistry

The cleavage of carbon-carbon bonds in the course of exhaustive chlorination of hydrocarbons was discovered by Krafft and Merz [1] in 1875 and first named "chlorinolysis" by McBee and his co-workers [2]. Nowadays the shorter term "chlorolysis" is used. If aliphatic hydrocarbons are chlorolyzed at normal pressure and temperatures of about 450 to 500°C, they mainly yield compounds such as carbon tetrachloride, perchloroethylene, hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, and hexachlorobenzene. Benzene and alkylbenzenes, however, are chiefly converted to hexachlorobenzene, which is cleaved only under stronger conditions.

Since about 1933 there has been activity in chlorolyzing hydrocarbons or their chlorinated derivatives, preferably those having two or three carbon atoms, to produce carbon tetrachloride and perchloroethylene [332]. The reaction conditions have usually been atmospheric pressure and temperatures of 500 to 700°C. Increasing the pressure up to 3.5 bar (1 bar = 14.503 lb/in. 2gauge) diminishes the yield of perchloroethylene to less than 30% [11]. Commercial operations already employ several variations of this process. Their disadvantages are the coproduction of carbon tetrachloride and perchloroethylene, limited flexibility (about 30 to 70% CCl₄), and the incomplete conversion of compounds with four or more carbon atoms. The by-product hexachlorobenzene has to be disposed of either through combustion or deposition.

A process to prepare exclusively carbon tetrachloride and hydrogen chloride by the chlorolysis of substances having at least two C-atoms requires the application of higher pressures to avoid the formation of compounds such as perchloroethylene or, in some cases, of soot. Based upon the equilibrium equation.



the amount of carbon tetrachloride converted to perchloroethylene at 600°C and 0 bar is calculated as 11.7% in contrast to 2.1% at 200 bar. Adding 2.5 mol of chlorine per mole CCl₄, the corresponding figures are 1080 and 5 ppm, which are decreased as the temperature is lowered.

The first suggestions regarding the possibility of producing carbon tetrachloride by the chlorination of aliphatic and aromatic hydrocarbons at high pressures and temperatures were made by McBee [3336] and Kung [37]. In developing this route to a commercial process, Hoechst began with benzene as the starting material [38]. Its chlorination results in 1 mol of hydrogen chloride

per mole of carbon tetrachloride, compared with 4 mol HCl from the chlorination of methane. Meanwhile, chlorinated aliphatics became increasingly available as by-products from the commercial chlorination of hydrocarbons such as methane, acetylene, ethylene, propylene, butadiene, cyclohexane, benzene, and toluene, or chlorohydrocarbons, e.g., 1,2-dichloroethane. In Table 1 some typical compounds in such residues are also listed as having a favorable ratio of C to H.

At the present time, aliphatic hydrocarbon wastes are preferred as feedstocks for the high-pressure chlorolysis plants in Frankfurt/Main.

The reaction equations in Table 1 show that for compounds with carbon-carbon multiple bonds the total number of moles decreases. It is only in this case that equilibrium depends on pressure. Hexachlorobenzene, for example, at 600°C and 0 bar yields 76.8% carbon tetrachloride in contrast to 97% at 200 bar. Furthermore, the rise in pressure at constant residence time increases the number of collisions and hence the space-time yield.

Chlorolysis is considerably influenced by the reaction temperature, which should not exceed 620°C to avoid excessive corrosion. This temperature limit is regulated by the excess of chlorine amounting to at least 20% of the stoichiometric quantity. The size of this excess depends on the temperature of the preheated chlorine needed for starting the reaction. Preheating up to 200°C may be necessary. On the other hand, compounds with carbon-carbon multiple bonds, e.g., dichlorobutenes, are first reacted with cold chlorine. The enthalpies of the exothermic chlorolysis reactions are generally sufficient for an adiabatic mode of operation. If the heat of reaction is too small to maintain this economical way of processing, e.g., in the case of hexachloroethane, it is necessary to add substances yielding higher reaction enthalpies.

The total rate of the numerous single reactions is given by the space-time yield. In chlorolyzing chlorinated aliphatic hydrocarbons at 200 bar and about 620°C, the space-time yield of carbon tetrachloride amounts to as much as 20 kg/l · h. Conversion is at least 95% per pass. The remainder consists mainly of hexachloroethane and hexachlorobenzene, which are recycled to the reactor. The reaction rate of aromatics is significantly lower.

TABLE 1 Chlorolysis of Hydrocarbons and Their Chlorinated Derivatives

	$-\Delta H_{\text{gas}}^{25^\circ\text{C}}$	
	kJ/mol	kJ/kg
$\text{CH}_4 + 4\text{Cl}_2 \rightarrow \text{CCl}_4 + 4\text{HCl}$	397	24,771
$\text{CH}_2\text{ClCH}_2\text{Cl} + 5\text{Cl}_2 \rightarrow 2\text{CCl}_4 + 4\text{HCl}$	445	4,500
$\text{CHCl}_2\text{CH}_2\text{Cl} + 4\text{Cl}_2 \rightarrow 2\text{CCl}_4 + 3\text{HCl}$	341	2,554
$\text{CCl}_3\text{CCl}_3 + \text{Cl}_2 \rightarrow 2\text{CCl}_4$	64	270
$\text{CH}_2\text{ClCHClCH}_3 + 8\text{Cl}_2 \rightarrow 3\text{CCl}_4 + 6\text{HCl}$	697	6,168
$\text{CH}_2\text{ClCH=CHCH}_2\text{Cl} + 10\text{Cl}_2 \rightarrow 4\text{CCl}_4 + 6\text{HCl}$	921	7,364
$\text{CCl}_2=\text{CClCCl}=\text{CCl}_2 + 5\text{Cl}_2 \rightarrow 4\text{CCl}_4$	402	1,540
$\text{C}_6\text{H}_6 + 15\text{Cl}_2 \rightarrow 6\text{CCl}_4 + 6\text{HCl}$	1,254	16,058



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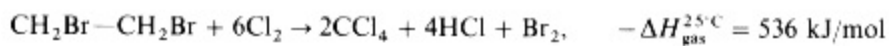
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TABLE 2 Chlorolysis of Oxygen-Containing Compounds

	$-\Delta H_{\text{gas}}^{25^\circ\text{C}}$ (kJ/mol)
$\text{CCl}_3\text{CHO} + 2\text{Cl}_2 \rightarrow \text{CCl}_4 + \text{COCl}_2 + \text{HCl}$	226
$\text{CO}_2 + \text{CCl}_4 \rightarrow 2\text{COCl}_2$	-55
$\text{H}_2\text{O} + \text{CCl}_4 \rightarrow \text{COCl}_2 + 2\text{HCl}$	61

Oxygen-containing organic compounds, e.g., alcohols, aldehydes, ketones, carboxylic acids, anhydrides, esters, ethers, epoxides, phenols, and quinones, are chlorolyzed to phosgene and minor amounts of carbon dioxide in addition to carbon tetrachloride and hydrogen chloride (Table 2). The carbon dioxide in the liquefied chlorine is partly converted to COCl_2 . Oxygen and water contained in the feedstocks are quantitatively reacted to phosgene and carbon dioxide.

Bromohydrocarbons, which may also be substituted by oxygen and chlorine, are transformed into carbon tetrachloride, hydrogen chloride, and elemental bromine as well as, optionally, into phosgene:



Process Description

A semicommercial chlorolysis plant, producing 8,000 t/yr carbon tetrachloride, has been operating successfully since November 1970 with hardly any mechanical difficulties. A commercial plant with a 50,000 t/yr capacity was started up in October 1976. Its flow sheet is shown in Fig. 1.

Liquid chlorine is compressed by a membrane or a special plunger pump to 240 bar max. Thereafter it is heated by high-pressure steam and combined with the chlorohydrocarbon feedstock before entering the reactor. The final temperature of the adiabatic reaction is maintained at 620°C max by the excess of chlorine. The reactor is heated electrically to start the chlorination. At the end of the reactor the products are quenched with cold carbon tetrachloride to a temperature of about 500°C. Expansion to 21 bar lowers this temperature to ~420°C due to the Joule-Thomson effect.

The chlorolysis products normally contain HCl , Cl_2 , CCl_4 , C_2Cl_6 , C_6Cl_6 , and possibly CO_2 , COCl_2 , and Br_2 when oxygen and bromine compounds are in the feedstocks. This mixture is separated in four columns.

In the heavy ends column a highly concentrated solution of hexachloroethane and hexachlorobenzene in carbon tetrachloride is recycled from the bottom into the reactor by a special plunger pump. The heat required is

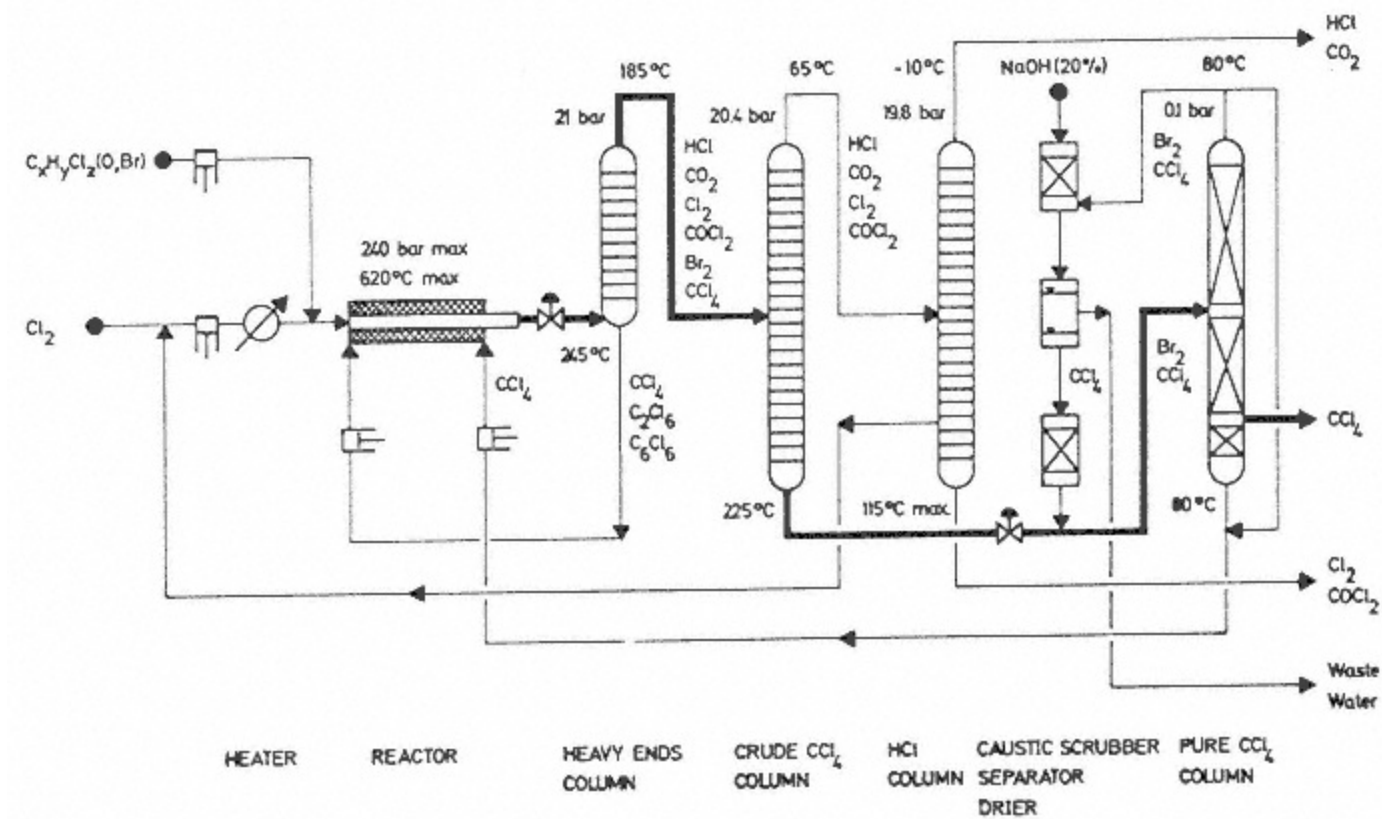


Fig. 1.
Chlorolysis process, Hoechst AG.

produced in a natural gas burner and transferred by circulation of aromatic hydrocarbons.

In the crude CCl_4 column, heated as described above, HCl , CO_2 , Cl_2 , and COCl_2 are drawn off at 20.4 bar and $\sim 65^\circ\text{C}$ into the HCl column. The carbon tetrachloride from the still bottom is refined in the pure CCl_4 column at normal pressure. The pure CCl_4 side stream is free of tri- and perchloroethylene and is therefore especially suitable for the production of fluorocarbons, e.g., CCl_3F , CCl_2F_2 , and CClF_3 . The bottom product is used as quench liquid for the cooling zone of the reactor. If the small quantity of head product contains bromine, it is fed into the caustic scrubber. The carbon tetrachloride is separated, dried, and recycled to the feed of the pure CCl_4 column. In the absence of bromine the low boils may be combined with the bottom product of this column.

The head product of the crude CCl_4 column, consisting of HCl , CO_2 , Cl_2 , and COCl_2 , is fractionated in the HCl column at 19.8 bar. Hydrogen chloride, drawn off at $\sim -10^\circ\text{C}$, contains only small amounts of carbon dioxide as a byproduct from the oxygen compounds of the feedstocks. Since this HCl is dry, it may be directly utilized in a hydrochlorination, oxychlorination, or electrolysis process. Liquid chlorine from the side stream is recycled to the reactor after being mixed with freshly liquefied chlorine. The bottom product consists of chlorine and more or less phosgene, depending on the composition of the feedstocks. This mixture can be used either in phosgene plants, oxychlorination processes, or in the production of sodium hypochlorite; otherwise it is fed into an incineration unit. Heat is transferred from the high-pressure steam to the HCl column by hexachlorobutadiene which is inert toward chlorine under the operating conditions of the still bottom.

Raw Materials

In principle, all hydrocarbons and their chlorinated derivatives which meet the following requirements are suitable as feedstock.

1. Solid materials, e.g., soot, coking products, or polymers, are not quantitatively converted to carbon tetrachloride and hydrogen chloride in the chlorolysis process. Because these components and nonvolatile inorganic compounds accumulate in the reactor, they must be separated by filtration or, in the case of solutions, through distillation, e.g., in a falling film evaporator. Volatile inorganic compounds such as iron(III) chloride tend to be deposited in the bottom of the heavy ends column and are filtered when the bottom product is recycled to the reactor.
2. Oxygen and oxygen-containing compounds may be tolerated to a certain degree, depending on their corrosion properties. Therefore the water content of the feedstocks should not exceed 100 ppm.
3. The concentration of sulfur and sulfur-containing compounds is limited to

25 ppm S in order to reduce the corrosion of the nickel tube; e.g., by intercrystalline attack.

4. Feedstocks containing up to 5% of aromatics (calculated as benzene) are smoothly chlorolyzed in the present type of reactor.

For environmental and economic reasons, residues from the production of carbon tetrachloride (based on methane), vinyl chloride, vinylidene chloride, tri- and perchloroethylene, 1,1,1-trichloroethane, allyl chloride, propylene oxide, chloroprene, hexachlorocyclohexane, chlorinated benzenes, and toluenes are preferred as raw materials.

In setting up the reaction equations of chlorohydrocarbon mixtures, the carbon and hydrogen contents are multiplied by 0.12807 and 0.36173, respectively, in order to obtain the amounts of carbon tetrachloride and hydrogen chloride produced (on a weight unit basis). The chlorine supply is calculated as the difference between the amounts of reaction products and feedstocks. The bromine content multiplied by 0.01 yields the quantity of Br₂. By this means a mixture of light and heavy ends from the manufacture of vinyl chloride monomer (VCM) with 27.9% C, 3.3% H, 68.7% Cl, and 0.1% Br is quantitatively chlorolyzed according to (numerical data in weight units):



For this raw material the stoichiometric usage per tonne carbon tetrachloride amounts to 0.280 t VCM and 1.055 t chlorine. In a specific design case the corresponding figures are 0.283 and 1.063 t.

Utility Requirements

The average utility requirements per tonne carbon tetrachloride, summarized in Table 3, include the usage of electricity and cooling water for the liquefaction of chlorine and for the emergency absorption of off-gases.

TABLE 3 Utility Requirements per Tonne CCl₄

Electricity	685 MJa
Natural gas	810 MJ
Steam: p = 13 bar	0.3 t
p = 2 bar	0.3 t
Cooling water, Δt = 10°C	75 m ³
a1 MJ = 0.278 kWh or 948 Btu.	

Typical Problems

One of the major problems during process development was to find a material resisting HCl, Cl₂, and CCl₄ at 240 bar max and 620°C max. Numerous corrosion tests with metallic and ceramic materials and intensive metallographic analyses of reactor defects showed that pure nickel is suitable, especially if certain limiting carbon and sulfur contents are not exceeded. Because of this and its ease in manufacturing, nickel is recommended as the material for commercial reactors. Seam and spot welds have not proved reliable.

Inadequate strength at 240 bar and 620°C necessitates jacketing of the unwelded nickel tube with high-temperature resistant steel. This steel must also be limited to low carbon and sulfur contents. Naturally the thermal expansion coefficients of both materials have to be matched as closely as possible. The state-of-the-art does not yet allow manufacturing of commercial reactors in one piece. Therefore lens-shaped high-pressure joints for the reactor sections had to be developed and jacketed with steel, too.

A further problem was pumping liquid chlorine in large quantities at pressures up to 240 bar. Today membrane and plunger pumps are used, the latter with a special stuffing box technique.

Summary

A process is described for the manufacture of carbon tetrachloride consisting of exhaustive chlorination of hydrocarbons and their chlorinated derivatives at 240 bar max and 620°C max [3946]. In this high-pressure chlorolysis less chlorine is consumed and consequently smaller amounts of by-product hydrogen chloride are formed than in the methane chlorination process. In contrast to similar operations at atmospheric or slightly elevated pressure, coproduction of other chlorinated hydrocarbons is avoided. As the amount of chlorohydrocarbon wastes increases, interest in this economic possibility of utilizing residues from the manufacture of chlorinated solvents and vinyl chloride monomer is growing.

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Clathrates and Other Inclusion Compounds

Everett J. Fuller

Introduction

Considerable interest in clathrates and similar systems has arisen over the past few decades. Scientifically, the extremely high shape-selectivity of inclusion compounds is attractive. Subtle shape differences between molecules can be sensed down to atomic dimensions. This is reminiscent of the high selectivities observed in studies of enzyme action, and indeed is explained in both instances by the same "lock and key" hypothesis of Emil Fischer: the two components must fit together as a key fits a lock or the clathrate (or enzyme-substrate complex in biological systems) cannot form. Clathration normally does not

involve chemical reaction, and therefore may be regarded as a simplification of the enzyme specificity problem. Components of clathrating systems are often much simpler molecular species than the high molecular weight protein enzymes, and consequently lend themselves to easier characterization; for example, by single crystal X-ray analysis. The analogy does not lead one directly to the solution of problems in enzyme action, so clathrate systems are normally studied as independent examples of molecular shape specificity.

Industrial interest in clathration is stimulated by the fact that shape-selectivity can apply to molecular species such as paraffinic hydrocarbons which are quite unreactive chemically. A rough correlation can be made in the petroleum business between the quality of the product and the degree of removal of long-chain paraffin molecules, as shown in Table 1. The discovery of urea-n-paraffin inclusion compounds [1] promised a major impact on a number of product lines, and was pursued actively toward that goal. At present, urea processing is quite limited in the petroleum business for three reasons. First, no large-scale use for the pure extracted n-paraffins (on the scale of 10 to 15% of a typical refinery throughput) is generally found. Second, conversion schemes such as isomerization or cracking can reduce the n-paraffin concentration in a typical stream without a yield loss. Finally, a refinery scale (of the order of 100,000 bbl daily) manipulation of solid urea introduces major solids handling problems. Of course, n-paraffins are not the only limitations to quality in any product; aggressive industrial research on clathration has nonetheless been productive of results, and it continues to the present time. Clathrate-type separations generally are not associated with high energy input (heats of reaction less than 10 kcal/mol). This may be a consideration in a processing environment of high energy cost when large-scale operations are introduced.

It is pointed out that molecular sieve zeolite separations have been successfully introduced to solve many problems once thought to be best done by urea processing. Clathrates and molecular sieves are both properly studied as inclusion compounds, but this discussion will be limited to systems which display no stable empty shape-selective crystalline structure. Comparisons will be made for purposes of clarity.

The mechanism of clathration is generally a crystallization of a solid

TABLE 1 Effects of Linear Paraffins on Product Quality

Product	Linear Paraffin	Results of Excess Linear Paraffins
Motor gasoline	n-Pentane to n-decane (n-C5 to n-C10)	Motor knock; poor fuel economy
Heating oil, jet fuel	n-C10 to n-C15	Poor flow at low temperatures
Light lubricating oil	n-C15 to n-C25	Poor viscosity behavior; cloudiness

"host" structure around "guest" molecules. A new solid phase is formed which incorporates both host and guest and is physically distinct from crystals of either. Powell [2] introduced the term "clathrate compound" to describe a particular type of molecular compound in which one component forms a cage structure imprisoning the other. Strictly speaking, the inclusion compounds formed by urea and n-paraffin molecules are not clathrates because the enclosures containing the guest molecules are channels or tubes, not cages. The distinction between these systems, which were designated as organic adducts by Fetterly [3], and true cage structures tends to diminish in clarity as more is learned about new systems. For example, thiourea channels display "zones of best fit" not found in urea channels. This does not constitute a true cage structure, but it illustrates the difficulty of being precise in nomenclature until the fine points of molecular positions are understood, as by means of X-ray crystallography. The more general term of "inclusion compound" is preferred [4] by this author, but popular usage has often settled upon "clathrate" even for the urea systems.

Historical Background:

Nature of Inclusion Compounds

The earliest known clathrate preparation was that of chlorine hydrate by Davy in 1811 [5]. The accurate description of the substance as a clathrate had to wait over a hundred years until X-ray techniques were developed which unequivocally describe the atomic positions in the crystal [6, 7]. Not until 1959 was the currently accepted formula of chlorine hydrate settled upon [8]; it was estimated as $(7.27 \pm 0.17)\text{H}_2\text{O} \cdot \text{Cl}_2$. The formula was nonstoichiometric: an explanation was supplied by Powell and co-workers in terms of two types of cavities in the hydrate structure, with all the large cavities and 20% of the small ones being filled with chlorine [9]. The molecular complexity of this system illustrates some of the phenomena often encountered in clathrate work: failure of the law of simple multiple proportions and considerable analytical difficulty in defining compositions. Considering the state of chemical theory at the time of Davy's work and for many generations afterward, it is not surprising that chemists sought to express the formula of chlorine hydrate as a simple whole number ratio of water to chlorine.

Bengen's discovery of urea inclusion compounds [1] provided one of the best known examples of the nonstoichiometry of inclusion compounds in systems where analytical definition of the compounds formed is much simpler than in the case of chlorine hydrate. For urea and its complexes with n-paraffins from 6 to 17 carbon atoms, Redlich et al. found

$$m = \text{moles urea/mole guest} = 0.65n + 1.51$$

where n is the number of carbon atoms [10]. This is unmistakably nonstoichiometric. It is a result of the absence of any normal chemical bonding between host urea molecules and guest paraffin molecules. Stability depends

instead on a fit of the guest into the host structure channel. Because the channel is uniform in dimension, it is not surprising that longer guests provide a close fit over more channel length, and therefore show higher stability in combination with urea, than guest molecules with carbon chains of, say, six carbon atoms.

Generalizations as to the bonding and stoichiometry of clathrates are difficult. The channel inclusion compounds formed between Werner salt compounds and aromatic hydrocarbons which were discovered by Schaeffer, for example, show a guest/host mole ratio of unity [11]. Possible strong molecular interaction between the host and guest seems to be ruled out by the X-ray evidence [12], which indicates an irregular channel with zones of maximum attraction or best fit with the guest, reminiscent of the thiourea inclusion compounds.

The IR spectroscopy of these clathrates, however, implies a weak charge-transfer interaction between host and guest molecules [13]. Chemical bonding between host molecules in the benzene clathrate of nickel 4-methyl pyridine thiocyanate is not indicated; stability is conferred by the operation of van der Waals forces between them. Urea or thiourea host structures are hydrogen bonded. It is evident that the various inclusion compound systems present a wide range of properties: bonding types and stoichiometry relationships in almost any conceivable combination are evident in known clathrates, and new phenomena are rapidly appearing. The postulate of no strong primary chemical bonding between host and guest is considered fundamental to the definition of these systems. For example, the highly selective complexing of aromatic molecules by copper(I) or silver(I) trifluoromethane sulfonic acid salts [14-17] defines the interface between clathration and complexing. Bonding between the metal atoms of the "host" to two alternate carbon-carbon bonds of the ring properly categorizes the system as a complex rather than a clathrate. Because the selectivity has not been observed in true solution, the existence of an extended crystalline lattice may be essential. This property is held in common with clathrates (the word clathrate is from the Latin *clathrus*, a lattice). Unquestionably, the great number of systems studied by de Radzitzky and coworkers, based on various derivatives of alkyl benzylamines in combination with nickel thiocyanate, includes examples of varying degrees of bonding between host and guest [18-21]. A charge-transfer interaction between aromatic nuclei of the host and guest has been proposed [20]; in the view of the present author, such an interaction is compatible with a clathrate system in which the primary host-guest interaction is steric in nature.

Examples of complexing systems which are not clathrates are soluble π complexes of metal salts and olefins or aromatics. A special case in classification arises in consideration of soluble cyclodextrin complexes. Conceptually there is nothing in our understanding of clathrate systems which says that they must be insoluble as such, although most clathrates are decomposed on dissolution. The so-called Schardinger dextrans [22, 23], which are large polysaccharide units obtained by the incomplete hydrolysis of starch, provide a large molecular cavity even when dissolved, so that clathration is retained in

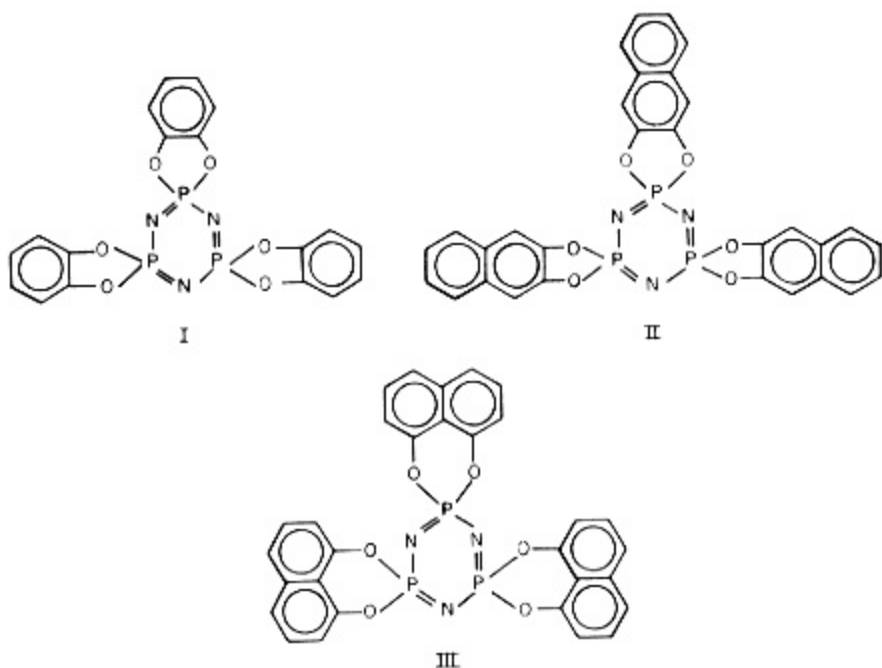
solution. Two recent developments of great interest as regards the liquid state and clathrationtype phenomena are the discoveries of the so-called "cryptates" [24, 25] and "liquid clathrates" [2628]. The cryptate systems utilize large ring polyether

ligand systems which solvate single metallic ions so that their solutions in solvents such as chloroform, ether, or benzene can be prepared and studied. The macrocyclic ligands can be synthesized to confer a high degree of size-selectivity on the metal ions solvated. New uses and applications of the cryptates abound, but their detailed discussion is outside the intended range of this work, which is limited to size- and shape-selective solid inclusion compounds. The liquid clathrates form between compounds of the general formulation $M[Al_2(CH_3)_6X]$, where M is an alkali metal or tetraalkyl ammonium ion, and X is azide, thiocyanate, selenocyanate, or halide ion and small aromatic molecules. They are nonstoichiometric and may contain as many as 16 aromatic molecules per anionic unit. Structurally, the systems appear to consist of either roughly spherical or layerlike domains which utilize the guest aromatics to help fill space. The "domain" construction would not appear to imply a high degree of molecular shape guest specificity as in the case of the Werner salt clathrates [11]. Liquid clathrate capacities for the xylenes have been measured; they are highest for o-xylene and lowest for m-xylene [29]. These systems are quite new; much remains to be learned in the area.

Clathrate System Discoveries

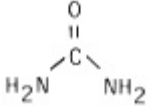
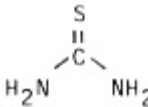
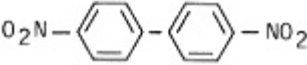
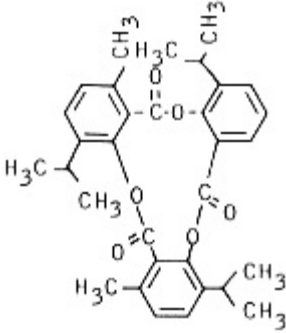
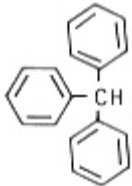

As the characterization of inclusion compounds grows in sophistication, more systems are found. In this section, some of the more interesting developments of the past 15 years will be cited as a general update to earlier exhaustive reviews of the subject [3, 9, 3033]. The reader is referred as well to review articles on specific topics, such as molecular interaction in clathrates [34], the nickel cyanide-ammonia clathrates [35], the clathrate hydrates [36], Dianin's compound [37], and aspects of separations techniques utilizing clathrates [38, 39].

The discovery and characterization of the channel clathrates formed by the cyclotriphosphazenes with a wide variety of organic guest species are examples of clathrate science which have been backed up since its inception by adequate X-ray crystal structure determinations [4043]. Stability of the benzene clathrate with tris(o-phenylenedioxy) cyclotriphosphazene (I) is much greater than with tris(2,3-naphthalenedioxy) cyclotriphosphazene (II). The X-ray work showed a minimum channel diameter in the former case of less than 5Å and in the latter case of 9 to 10Å. The larger channel dimensions and lower stability allow the onset of molecular "tumbling" by guest benzene molecules above -40°C [42]. p-Xylene clathrated by tris(1,8-naphthalenedioxy) cyclotriphosphazene (III), on the other hand, is firmly fixed in position by channel constrictions [43]. Selective incorporation of noncyclic molecules in mixtures of guests by I was observed as was displacement of clathrated benzene by an excess of xylene or carbon disulfide. This class of host system shows no strong bonding between host molecules. The packing of the large "paddle wheels" of the host can lead to solid structures which fill space less efficiently than if guests are incorporated to form a clathrate. Analogy with the "liquid clathrates" of Atwood [2629] is obvious, and extension of this approach to new clathrate

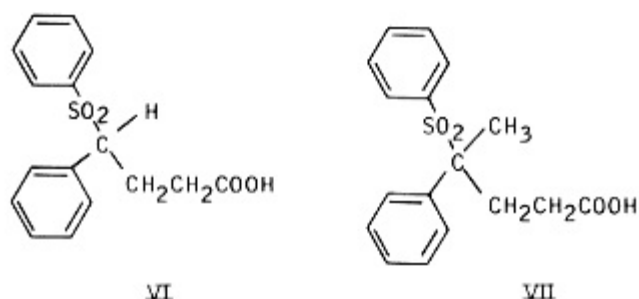
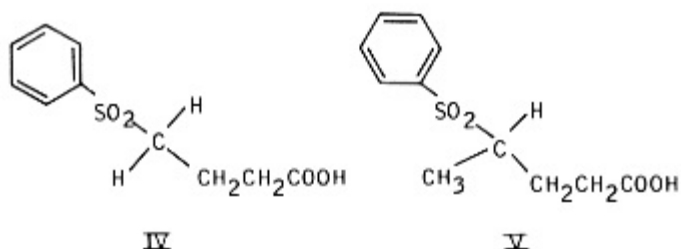


systems has been demonstrated. For example, the crystal structure of the clathrate $K[CH_3Se\{Al(CH_3)_3\}] \cdot (benzene)_2$ has been determined [29]. The two benzene guests are crystallographically independent. Generation of large molecular units which might pack easier in the form of clathrates represents a significant step toward deliberate synthesis of clathrates. Historically, the discovery of new systems has been accidental since no technique exists to predict crystal packing arrangements in advance. Of course, structural modification of known clathrating systems generally succeeds, depending on how much the systems can be strained, but the prospects of some predictability in clathrate synthesis are exciting. The structures of a number of known clathrate hosts, in addition to the cyclotriphosphazenes, fall into the "threebladed paddle wheel" category as pointed out by Allegra et al. [50] and as shown in Table 2. That this line of thought is of limited generality is evident by the clathrating ability of 4,4'-dinitrodiphenyl and many other nontriangular systems, and by the failure of many obvious candidates to clathrate. For example, the synthesis of a series of 4-(phenylsulfonyl) carboxylic acids (IV through VII) produced a clathrating system only in the case of VII [52]. In this series the utilization of the carboxylic acid moiety as the third "blade" may depend on its exclusion from a preferred position in the crystal by the methyl group. X-ray data might resolve this point, as well as the question of whether the clathrates are of the cage or channel form. If the system behaves as an analog of the triphenylmethanes, it should clathrate in a channel form. Guest species identified were diethyl ether, carbon tetrachloride, benzene, toluene, cyclohexane, and n-heptane. Selectivity for long-chain guests was not reported; this would be an indication of channels by extension of the work on the cyclotriphosphazene clathrates [40].

TABLE 2 Some Channel Clathrate Host Substances

Host	Structure	Guests	Channel Diameter (Å)	Refs.
Urea		n-Paraffins	5.2	3,44
Thiourea		Isoparaffins, cycloparaffins	6.1	45
4,4'-Dinitrodiphenyl		n-Paraffins	5	46
Tri-o-thymotide		n and Isoparaffins	4.86.9	47
Triphenylmethane		n- and Isoparaffins	~6	48
Perhydrotriphenylene		Rare gases, n-paraffins, aromatics, high polymers	~6	4951

Perhydrotriphenylene clathrates an unusually broad spectrum of guest substances [4951]. Barrer [33] has noted that the lack of strong host-host bonding correlates with a tendency of the host lattice to change with the shape and size of guests, sometimes producing more than one kind of clathrate structure (i.e., cage structures for small guests and channels for long guest

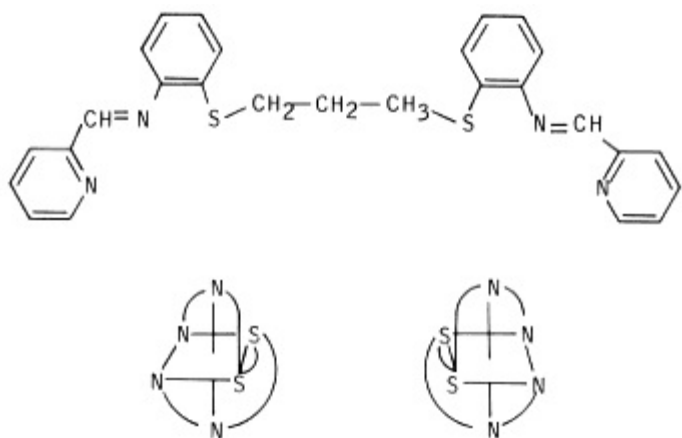


molecules). This behavior is shown in tri-*o*-thymotide clathrate systems, and would be expected for 4,4'-dinitrodiphenyl and cyclotriphosphazenes as well.

The extent to which a clathrate host can be modified without loss of the clathrate-forming tendencies remains a problem to be solved by trial and error. Gawalek and co-workers have shown that clathration of aromatics by $\text{Ni}(\text{CN})_2\text{NH}_3$ [53] can be extended in scope by substitution of a number of amines for ammonia [54]. The amines included methylamine, *n*- and isobutylamines, dimethylamine, and aromatic amines such as 2- and 4-methylpyridines, 4-*n*-propylpyridine, and 2,6-lutidine. Pyridine itself did not form clathrates when substituted for ammonia, although it does clathrate with $\text{Ni}(\text{CN})_2\text{NH}_3$ as a guest species. Other examples of host structure modifications which clathrate are the thio analog of Dianin's compound [55]; the dihydroxy derivative of triphenylmethane [56]; substitution of other metal atoms for nickel in the $\text{Ni}(\text{CN})_2\text{NH}_3$ ·benzene clathrate [5760]; a large number of modifications of the Werner compound clathrates using a divalent metal ion, an organic amine, and a monovalent anion such as thiocyanate in combination to form a host substance [11, 1821]; and the substitution of sulfur or selenium for oxygen in urea to produce clathrate compounds displaying selectivity properties quite distinct from those of the urea clathrates [6164]. The crystal structures of many of the modified clathrate systems have not been reported. For example, the substitution of 4,4'-dipyridyl for 4-methylpyridine in the Werner salt clathrates $\text{M}_{\text{II}}(\text{amine})_4(\text{SCN})_2$ may bring on a drastic structure change [65]. The modified clathrate is selective for *o*-xylene and indene, while the 4-methylpyridine host is highly selective for *p*-xylene. Some expansion of the host lattice by the introduction of a larger amine would be expected even if the essential structure were unchanged, but the diamine structure provides more bonding opportunities with the metal atoms, which should be explored

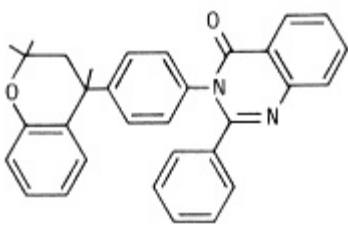
crystallographically. 4,4'-Dipyridyl appears in another clathrate system utilizing nickel(II) ethylxanthate and various heterocyclic amines [66]. The 4,4'-dipyridyl derivative clathrates p-xylene much more strongly than the other C₈ aromatics [67]. Intermolecular bridging between nickel atoms is expected with 4,4'-dipyridyl, but the adduct of nickel ethylxanthate with 1,10-phenanthroline also clathrates 1 mol of guest per mole of nickel, and both amine derivatives clathrate benzene and chloroform. The guest preferences differ otherwise, so it is probable that two distinct host systems, rather than two modifications of the same host, exist. Intermolecular bridging is also suggested by the announcement of a separation of the isomeric trimethylbenzenes using clathration by Ni^{II}(N,N-dimethyl-p-phenylene diamine)₂ or 4(SCN)₂, with the additional puzzle of an apparently variable amine stoichiometry [68]. X-ray powder pattern data taken by Casellato and Casu imply two distinct clathrate phases for Ni^{II}(4-methylpyridine)₄(SCN)₂ clathrates, which appear not only as a result of a change in guest species but even for the same guest [69]. Styrene, for example, could be clathrated in the usual β -form, with a guest/host mole ratio of unity, or in a different " γ " form with more than one aromatic ring of guest per host unit. The more unstable form of styrene clathrate was the γ -form, as shown by its conversion to β -form clathrate on standing at room temperature. For polynuclear guest aromatics such as p-terphenyl, the γ -form was preferred.

Synthesis and characterization of relatively large and rigid molecules has led to new clathrate systems. Because clathrate guest species can fill space packing deficiencies, this is not surprising. For example, the metal complexes of the sexadentate ligand, 1,5-bis[2-(2 pyridylmethyleneimino)-phenyl]-1,5-dithiapentane, which occur in the two enantiomeric configurations shown,



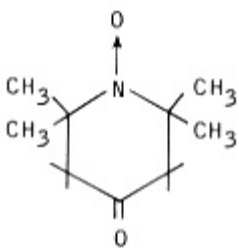
will clathrate one or more molecules of water, alcohol, dimethylformamide, or acetone [70]. The incorporation of polar solvent molecules into the lattice by clathration must be distinguished from direct complexation (e.g., hydrates of salts such as copper sulfate). In this case the IR data indicated that the acetone molecule was not coordinated to the metal ion. An example of a large host molecule not containing any metal ions is 3-p-(2,2,4-trimethylchroman-4-yl)-

phenyl-2-phenyl-4(3H)-quinazolinone [71]:



The clathration of cycloparaffins from cyclopentane to cyclooctane was observed. The selectivity is similar to that of thiourea, but differs in that benzene is clathrated in this case. *tert*-Butyl and isobutyl, but not *n*- or *sec*-butyl alcohols, are guests. The large beryllium oxybenzoate molecule, $\text{Be}_4\text{O}(\text{C}_6\text{H}_5\text{COO})_6$, will clathrate aromatics when precipitated out of solution [72]; it displays *p*-xylene selectivity among the C_8 aromatic isomers. Two molecules of host were shown to clathrate one xylene molecule [73].

The clathrates of mainly linear molecules utilizing 2,2,6,6-tetramethylpiperid-4-one-1-oxyl [74] are mentioned as an example of a relatively low molecular weight host unit which has been discovered since 1960, and to illustrate the diversity of possible clathrate systems.



Operational Aspects of Clathrate Separations

The preceding material demonstrates that a wide variety of clathrate systems is available, that a good many separations otherwise difficult to achieve may be accomplished using clathrates, and that fundamental discoveries of clathrate systems are appearing with increasing frequency.

In this section, some of the properties of clathrate systems which have a direct impact on their use as separating agents will be discussed. By the nature of clathration, the selectivity for a desired guest may be very high; that high selectivity alone is not the answer to the requirements of the separations analyst is evident in that clathrate processing is not an industrially prominent operation at present.

The equilibrium nature of clathrate formation and declathration has major implications in a separation scheme. For a mole of clathrate $\text{H}\cdot\text{G}$ which

decomposes into a mole of host, H, and a mole of guest, G, we write the reaction for declathration:



The equilibrium constant for dissociation is

$$K_{\text{dissoc}} = \frac{a_{\text{H}} \cdot a_{\text{G}}}{a_{\text{H} \cdot \text{G}}} \quad (2)$$

where a represents the activity of the species. Now for a solid clathrate which forms only one crystallographically distinct phase at standard conditions (say 25°C and 1 atm) with guest G of defined stoichiometry (host/guest ratio of unity in the present case), we have described the standard state for the solid clathrate phase, i.e., $a_{\text{H} \cdot \text{G}} = 1$. Then,

$$K_{\text{dissoc}} = a_{\text{H}} \cdot a_{\text{G}} \quad (3)$$

The treatment so far does not describe the nature of the host phase. Detailed theoretical consideration of clathrate systems [7577] is done by a stepwise conversion of the host from its initial equilibrium guest-free phase, designated the α -phase, to an empty clathrate β -phase, to filled clathrate on addition of guest:



The β -phase stability can be important in separations, as will be discussed later. Essentially, the β -phase would have all the host molecules in the same positions as if guest molecules were present. The impact of the β -phase on the system will depend on its equilibrium stability relative to the α -phase and on kinetic factors; a slow transformation to α -phase in the absence of guest may facilitate the use of an empty β -phase. Equilibrium theory does imply activity contributions from all three phases: there will always be some α -phase and some empty β -phase present, although the stability of $\text{H} \cdot \text{G}$ clathrate may be high enough to make analytical detection of them difficult. For present purposes we shall consider clathration to be the sum of Reactions (4) and (5). Then a_{H} refers to the activity of the host α -phase. If it is present in excess as pure solid in its standard state, we have $a_{\text{H}} = 1$, and

$$K_{\text{dissoc}} = a_{\text{G}} \text{ (excess host)} \quad (6)$$

Equation (6) is usually the basis of analytical determination of clathrate equilibrium constants. One measures the activity of uncomplexed guest when both clathrate and host are present in equilibrium. This may be approached using the guest in the gas phase, in which case it is convenient to measure the vapor pressure, P_{G} , of guest above a mixture of host and clathrate. If the vapor

is ideal, the fugacity is P_G/P° , where P_G° is the equilibrium vapor pressure of guest, and

$$K_{\text{dissoc}} = \frac{P_G}{P_G^\circ} \quad (\text{where } a_H = 1) \quad (7)$$

A dew point apparatus has been devised by Redlich and co-workers which is useful for equilibrium constant determinations, especially if the guest is quite volatile [10, 78]. Alternatively, the activity of the guest may be approximated by its mole fraction X_G in an ideal solution of a nonclathrating solvent. Then,

$$K_{\text{dissoc}} = X_G \quad (\text{where } a_H = 1) \quad (8)$$

Of course, Eq. (2) may be used as the basis for determining equilibrium constants if a_H is not unity, provided its value is known. Equation (8) has a special significance for clathrate separations. The equilibrium constant represents the lower limit to which G can be removed from solution in a nonclathrating solvent by making pure clathrate $H \cdot G$. The situation is represented schematically in Fig. 1. Guest may be added to a mixture of solvent and host, starting at A and proceeding to B , with no formation of clathrate. At Point B the concentration of guest in solution defines the equilibrium constant where host, clathrate, and guest at constant activity may coexist. As additional guest is added, the host will form clathrate along segment BC , until at C all the available host is utilized. Additional guest appears in solution. The length of BC depends on the amount of host in the system. Because Fig. 1 is a stable equilibrium diagram, it does not show the hysteresis behavior common to many clathrate systems on loading and unloading. The isotherm ABC should be determined experimentally from both directions, but it must be remembered that the solution, chosen to approximate ideality with respect to the guest, will usually interact so slightly with the host that the interconversion of host and clathrate solid phases will be very slow, and will be complicated by supersaturation, particle size dependence, and similar phenomena. These problems are often solved by addition of a small amount of "catalyst" solvent which dissolves some of the host phase.

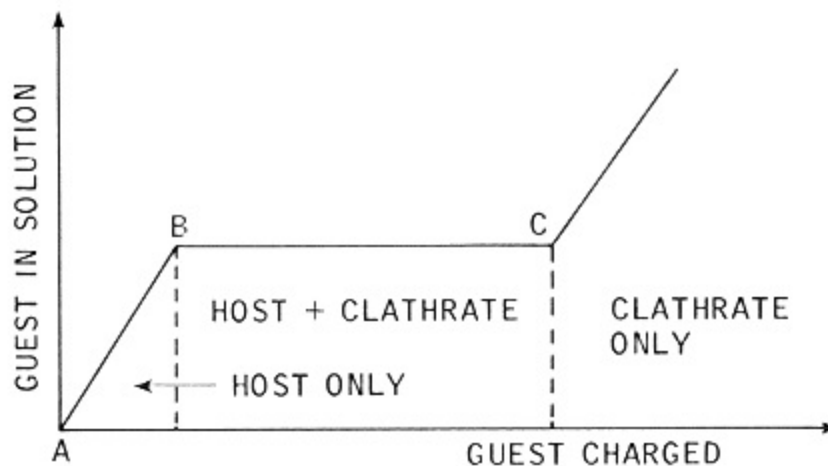


Fig. 1.
Clathration equilibrium limitation.



Fig. 2.
Host system with permanent
cavities.

The solid phases can then be transformed through the relatively fast process of dissolution-reprecipitation. Isotherms of the type shown in Fig. 1 have been observed in studies of interaction between vapor-phase aromatic molecules and solid potassium benzene sulfonate [79], between vapor-phase aromatic hydrocarbons and $M_{(II)}(4\text{-ethylpyridine})_4(\text{SCN})_2$ [80], and between liquid aromatic hydrocarbons and various clathrating agents [21, 81]. It is probable that a small host solubility in the liquid aromatic guest provides kinetic assistance in the case of some of the Werner salt host clathrates, so that the equilibrium curve may be defined without the addition of polar "catalyst." The isotherm which would be expected if the clathrate were formed by simple filling of an empty β -phase is shown in Fig. 2. This behavior corresponds to that shown by zeolite systems which possess a permanently porous structure. Guest appears in solution only after complete filling of the cavities in the solid; and guest may be removed quantitatively from solution by the host because no equilibrium limiting activity of guest is needed to stabilize the cavity-containing β -phase. In practice, the use of clathrate β -phases is often beset with problems of metastability (collapse into the α -phase) or diffusion limitations. Clathrates which imprison the host substance by three-dimensional cages rather than channels pose the problems of how the β -phase could be prepared without damage to the cages, and if prepared, how such a phase could be used without cage destruction. Some of the same considerations are evident in channel clathrates, wherein the structural features which lead to the high selectivity characteristic of clathrates may also imply a poor diffusion rate of feed mixture species through a pre-formed crystal. The use of β -phases is a new and exciting aspect of clathrate operations and will be discussed later.

Although the selectivity of clathration is often very high, the separation factor, defined by

$$\alpha = \frac{[G_1/G_2]_{\text{clathrate}}}{[G_1/G_2]_{\text{liquid}}} \quad (9)$$

for the clathration of two guests from a liquid mixture, is not generally infinite. Thus it is commonly observed that a given host forms clathrate with a number of guests. This means that the separation may have to be carried out over more than one stage of clathration to achieve the desired product purity. Operationally, we must define the equilibrium between host H and mixed guests G_1

and G₂ so as to examine the implications for process design. Two limiting cases exist: one clathrate solid containing both guests, or two distinct solid phases. A distinction between these alternatives is readily made if the separate equilibrium constants are known. Excess host is equilibrated with a solution of both guests, and the activities of the two guests are measured in the presence of solid clathrate and host ($a_H = 1$). If G₁ and G₂ are in different clathrate phases (for clathrates H·G₁ and H·G₂),

$$K_1 = a_{G_1} \quad \text{and} \quad K_2 = a_{G_2} \quad (10)$$

If a mixed clathrate phase is present, the guest activities will in general fall below K_1 and K_2 . The solid solution behavior is described by

$$\frac{a_{G_1}}{K_1} + \frac{a_{G_2}}{K_2} = 1 \quad (11)$$

A rationale for the experimental observations described by (11) is based on the assignment of guest activities in the mixed clathrate. If the activity of i -th guest in clathrate is taken as its mole fraction in the extract, Y_i , then

$$K_i = \frac{a_{G_i} a_H}{Y_i} \quad (12)$$

for each guest. Equation (12) implies an ideal solid solution mixed clathrate; careful work in phase definition is necessary to define the limitations of its use. The same properties of clathration which lead to high selectivities may imply highly nonideal mixed clathrate solids. The test for this is an examination of the selectivity (Eq. 9) over a range of ratios of G₁/G₂ in the charge mixture. If α is observed to be quite constant with respect to large changes in charge composition, it may be assumed that (12) is valid. Then

$$Y_1 + Y_2 = a_H \left(\frac{a_{G_1}}{K_1} + \frac{a_{G_2}}{K_2} \right) = 1 \quad (13)$$

When $a_H = 1$, (11) follows. The separation factor α is fundamentally defined as the ratio K_2/K_1 . If the liquid is an ideal solution ($a_G = X_G$, the mole fraction) and the guest activity in the solid can be represented by Y , then for unit host activity

$$\alpha = \frac{K_2}{K_1} = \frac{Y_1/Y_2}{X_{G_1}/X_{G_2}} \quad (14)$$

The summation $\sum_i (X_{G_i}/K_i)$ is useful in predicting the results of a clathration experiment if the charge mixture mole fractions are used. Obviously, if $\sum_i (X_{G_i}/K_i) < 1$, no clathrate will form, and if the summation is greater than unity, clathrate will or will not appear at equilibrium depending on a_H . The term is therefore a measure of the supersaturation with respect to guests.

The foregoing discussion on mixed clathrates is the basis for the common and extremely useful cocrathration effect. Some of the applications of cocrathration will be cited as a means of clarification [3, 10, 82].

- (1) Clathration below the normal equilibrium limit of a guest may be easily accomplished if a second guest is present. The requirement is the existence of mixed clathrate. If problems of solid-phase nonidealities do not intrude, G_1 , may be completely removed from solution by cocrathration with G_2 , as shown by plotting Eq. (11) in Fig. 3. High clathration recoveries are achievable not only by means of high clathrate stability for desired product, but also by suitable choice of a cocrathrating agent. The cocrathrator may be selected to perform other functions as well [83, 84], as will be discussed in a later section.
 - (2) Clathration of a normally nonclathrating guest follows directly from what has been stated. In this case $K > 1$, and clathrate must be stabilized by another guest. It is emphasized that such a cocrathration is operationally distinct from use of the empty β -phase to incorporate normally nonclathrating guests in that stable mixed clathrate is obtained from initial α -phase.
 - (3) Convenience in estimating equilibrium constants for a series of guests may result from the ordinarily rapid clathration of mixtures with a guest whose equilibrium constant has been independently defined. Care should be taken to ensure that the α values experimentally obtained by analysis of the solid and the unclathrated guest mixture are realistic indications of relative equilibrium stability (Eq. 14) and do not reflect nonideality in the phases. As indicated, the constancy of α over a range of charge compositions is a reliable check on this.
 - (4) Contamination of the extract is a problem even when operating with high selectivity (see the section entitled "Some Processing Examples" below), but it is aggravated by cocrathration. For this reason it is vitally important, when evaluating a clathrate system for any proposed separation scheme, to check the clathrate selectivity in the presence of all possible contaminants. Furthermore, it is probable that the driving force for cocrathration will be greatest where the concentration of the desired product is at a minimum, i.e., at the point where the clathrate is in equilibrium with the fully depleted feed mixture. Provision must be made in the scheme for removal of cocrathrated impurities, either by reclathrating or by some exchange scheme.
- The common nonstoichiometry of clathrate systems implies that Eqs. (1) through (14) must usually be corrected for the prevailing mole ratio of host to

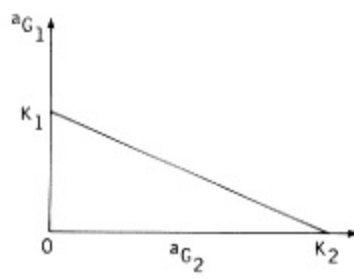


Fig. 3.
Coclathration.

guest, m:



$$K_{\text{dissoc}} = \frac{(a_H)^m \cdot a_G}{a_H \cdot (G)_m} \quad (2')$$

and

$$K_i = \frac{a_{G_i} (a_H)^{m_i}}{Y_i} \quad (12')$$

For the case of host activity which is not unity, the ratio of equilibrium constants is

$$\frac{K_2}{K_1} = \frac{Y_i/Y_2 (a_H)^{m_2 - m_1}}{X_{G_1}/X_{G_2}} \quad (15)$$

which reduces to (11) for unit host activity or if $m_2 = m_1$ [10].

It must be kept in mind by the experimentalist in the clathration field that we are usually dealing with changes in the solid state. Rates of solid-phase transformations can be too low to be of interest, even when the driving force for an equilibrium change is large. For example, solid urea can be mixed with n-cetane without reaction at room temperature [3], although the urea-n-cetane complex is extremely stable. Addition of a drop of methanol to solubilize the urea results in formation of the complex. The rate processes of primary interest are clathration, declathration, exchange, and phase change in the host. Clathration and declathration are the reverse and forward directions of (1), and phase change is Eq. (4). The exchange reaction (for host/guest ratios of unity) is



Clathration ordinarily involves a total change of phase in the solid state from α -phase to loaded β -phase. The crystal structures can be quite different so that the growth of clathrate solid is observed microscopically along with the disappearance of host crystals. If clathration from solution of dissolved host and guest is observed, the precipitation of clathrate is quite fast. Manning and coworkers [8590] have found the formation of urea adducts under these conditions to be rate-limited by diffusion in the liquid. The work of Fetterly [3, 91] on the kinetics of urea adduction from aqueous solution showed microscopically that adduct was formed in the aqueous phase, not in the interface or the hydrocarbon bulk phase. Many substances which change the nature of the hydrocarbon-water interface, and therefore alter the rate of passage of guest from the nonaqueous to the aqueous phase, had a profound effect on the kinetics. Polar additives such as alcohols or ketones improved the clathration rate, while many soaps, hydroperoxides, or sulfur compounds lowered it drastically [92]. Because these effects vary from one guest to another, they may be utilized to obtain unusual nonequilibrium selectivities [3]. The inherent stability of clathrate relative to host means that the rate of dissolution of

clathrate may be slower than the rate of dissolution of host and that the equilibrium solubility of host is higher if no guest is present. These features lead to nonequilibrium effects which are only beginning to affect the science and technology of clathration, and whose eventual impact may be quite significant. The polar hosts urea and thiourea tend to "salt out" hydrocarbon from solution in the phase where reaction probably takes place; it was observed that mixing solutions of host in polar solvent with solutions of hydrocarbon in the same solvent gave a higher adduct yield in a few minutes than if the same proportions of charge substances were mixed simultaneously [93]. Presumably the nonsalted-out initial guest concentration and therefore the driving force to produce adduct was higher in the former case. This work used 2-methoxyethanol as solvent and urea or thiourea as host. The hydrocarbon mixtures were cyclohexane (a guest for thiourea) and n-heptane or n-octane (urea guests). The solvent capacity for the hydrocarbons is much greater than in the aqueous studies of Fetterly, and the hosts were shown to exert powerful salting-out effects [38, 94]. Again, the selectivities could be manipulated by nonequilibrium effects (rate of adduct formation, rates of salting out, and low adduct dissolution-reprecipitation rates). The selectivity changes observed by Fetterly were considered to be the result of differences in rates of crystal growth for various guests, and not differences in the amount of solid clathrate. Especially with regard to nonaqueous polar solvent systems, the use of nonequilibrium effects is in its infancy. Clathration rate studies of the Werner salt systems $\text{MP}_4(\text{SCN})_2$, where M is a bivalent transition metal ion and P is 4-methylpyridine or 4-ethylpyridine, have usually been done with solid host stirred in a liquid phase. Gawalek and Könnecke showed that clathration could be easily followed by microscopy in these systems and found that lower rates of clathration (around 1 h to completion) were associated with low solubility of host crystal in the aromatic liquid [95]. This was directionally confirmed by Minton and Smith, who diluted the guest with paraffin in which the host $\text{Ni}(\text{4-methylpyridine})_4(\text{SCN})_6$ would be quite insoluble [96]. They found clathration times as long as 48 h at room temperature from highly diluted (0.16 mol/l) guest solutions. Jacobs and Lok held the guest concentration in heptane constant and varied temperature, metal ion, and guest aromatic, using metal thiocyanate-4-methylpyridine combinations [97]. The rate of clathration did not change significantly from 20 to 42°C, nor on varying the guest aromatic from benzene to toluene to p-xylene. The conditions led to p-xylene clathration times up to 16 h at 25°C, with the rates for various metal ions decreasing in the order $\text{Co} > \text{Ni} > \text{Fe} \gg \text{Mn}$. Because most of these results are complicated by solubility of the host crystals, it would be of interest to study relative rates of filling of an initially empty β -phase by gaseous guest species, since it has been shown that the $\text{M}(\text{4-methylpyridine})_4(\text{SCN})_2\beta$ -phase can be well characterized [69, 80].

In general, considerable simplification with regard to the number of components is afforded by kinetic studies of the interactions between solid hosts and guests in the gas phase. However, the situation is complicated by the difficulty of nucleating the new clathrate phase in the absence of any dissolved host, and possibly by the coating of the

α -phase surface by clathrate. Allison and Barrer [98] have studied the rates of clathration of various guests with phenol and quinol, and report induction times indicating the difficulty of

nucleation of clathrate phase. An interesting catalytic effect of shaking the host crystals with steel ball bearings was observed; reaction did not normally occur in the absence of shaking. The same effect was observed earlier for formation of gas hydrates from ice crystals and xenon at -78°C [99, 100]. In both these systems the shaking served to break off layers of clathrate from the surface so that fresh reactant α -phase was continually exposed. The studies on phenol and quinol also indicated that the host crystals when shaken in vacuo were disordered relative to the α -phase in such a way that clathrate nucleation on subsequent exposure to guest was facilitated. A mechanical effect on the rate of urea adduction from mixtures of hydrocarbons was observed by Spengler and Braun [101] who used vibration frequencies up to 104Hz. This was done in solution and is therefore difficult to compare with the gas-solid work. No mechanical agitation is described in the work of McAdie and Frost, for example, who studied the solid urea-n-octane vapor system and found no evidence for adduct formation after 24 h at room temperature. They initiated adduction by admitting water vapor [102]. After decomposition of the adducts under vacuum, reaction with n-octane vapor could take place without water vapor initiation. It is noteworthy that both mechanical vibration and declathration can shatter crystals and provide a large surface area, which would be expected to improve the rate of a gas-solid reaction. Experiments on host solid obtained by declathration often lead to the proposal of the existence of empty β -phase. Rate studies of the β - α transition are rare, probably because the reaction is ordinarily completed by the time strongly clathrated guests are removed. The preparation of guest-free β -phase is approached by vacuum removal of guest from as unstable a clathrate as can be obtained [69, 80]. In the case of the metal thiocyanate-4-picoline Werner salt clathrates, such a guest is benzene. The X-ray power patterns before and after complete removal of benzene by vacuum were shown to be the same, and distinct from the pattern exhibited by the α -phase. Conversion to the stable α -form in this system is accompanied by loss of amine, as shown by thermogravimetric analysis [69]. $\text{Ni}(\text{SCN})_2(4\text{-picoline})_4\beta$ -phase begins to lose amine at around 125°C and the β - α phase transition takes place at 130°C . The rate of this change is obviously important only under conditions where the β -phase is itself being studied; commonly the solid phases of interest are α -phase and clathrate.

The kinetics of the guest exchange reaction (16) have been studied by only a few investigators. Schlieff and Leibnitz [103] showed that n-octadecane at 30°C could replace 50% of the n-decane from an initially pure n-decane urea adduct in 40 min. The test conditions implied considerable dissociation of decane adduct followed by clathration of the octadecane. Exchange of n-decane for adducted n-hexacosane did not occur, nor was appreciable displacement of n-decane observed in the absence of benzene diluent. The mechanism of exchange was concluded to be declathration-reclathration. It is expected that the same mechanism will prevail in the majority of clathrate systems: if a three-dimensional cage structure exists around the guest molecules, declathration without cage destruction is unlikely, and if a channel system exists, the statistics of a strictly diffusion

exchange imply a prohibitively slow rate to equilibrium in channels longer than the length of 10 guests or so. The solid clathrate structure once set up does not ordinarily permit guest motion throughout; this is in

contrast to the molecular sieve structures. Not only are the molecular sieves immobile as to dissociation-recrystallization under normal operating conditions, but they present more options for guest motion between cages, supercages, etc. [104]. The author [38] found that exchanges between thiourea guests in slurries of 2-methoxyethanol were accelerated in rate by an increase in solubility of the guest being displaced, indicating that transport of guest into solution from the adduct being dissociated was rate-limiting. In this system the host solubility is quite high, and over 60% completion of the exchange reaction was indicated in 5 min at room temperature. Exchange of guests in the $\text{Ni(4-picoline)}_4(\text{SCN})_2$ aromatic hydrocarbon clathrates was first noted by Belitskus et al. [105]. They reported exchange without any morphological change in the crystals, even for guests in which the host was quite insoluble. No kinetic data were reported. Because the incoming guests were added in hexane solution, the possibility of declathration of the original guest by equilibration with the liquid exists. The experimental challenge of unambiguously determining the mechanism of a clathrate exchange reaction is formidable. For liquid-solid systems work, one could propose a diffusion mechanism as opposed to declathration-reclathration only if clathrate dissolution and declathration by guest dissolution into the added liquid phase were both eliminated as factors in the exchange. Low equilibrium host solubility does not preclude a fast passage of solid through the dissolved state. Even if the initial and final guests both form clathrate, one must either show that the two clathrate phases are the same (except for guest) or maintain enough of the initial guest in the added solution to stabilize starting clathrate before concluding that declathration is not occurring. For any practical use of clathrate exchange the mechanism may not be critical, if by acceptable means the desired rate can be achieved. Clathrate selectivities are so high relative to those of many other separation schemes that at least rough separations may be made with only one clathrate equilibration. The processing requirements of high purity of clathrated product and/or nearly complete recovery of that product from the feed mixture imply multiple equilibrations, which are facilitated by fast guest exchange, as will be discussed later.

Some Processing Examples

Clathrate properties are readily demonstrated in simple laboratory tests. Once the essentials of a separation scheme have been demonstrated in the laboratory, the task of adaption to an industrial process begins. This may be an extension of existing operations if, for example, the separation is to be part of an analytical scheme [106] or if the product sought is of high value and the operational scale is sufficiently small. Such cases will not be dealt with in this discussion, although they represent an important area of clathration technology, because in the author's opinion few new problems are generally met, which are not already dealt with in the course of laboratory characterization of clathrates.

In this section, some of the special problems of larger scale continuous unit

operations will be discussed. Because each clathration system presents a different set of properties, the features will be described with reference to specific separations, either presently operational or at some preliminary stage of development. Detailed description of the various processes will not be attempted; rather, an overview will pick out the salient points so that the reader may hopefully grasp the "state of the art" of clathration processes as an entirety.

The first obstacle to large-scale use of clathrates in a separation scheme is that, as a rule, the manipulation of the solid phase becomes necessary. Strictly liquid-phase clathration presents an obvious way out of this, but such phenomena are quite rare at present. Mention has already been made of the cyclodextrins, the cryptates, and the "liquid clathrates." A process for recovery of aromatic hydrocarbons from mixtures containing them could utilize a liquid-liquid extraction with an aqueous cyclodextrin solution, in principle. In fact, the solubilities of the aromatic clathrates are so low that the extractant solution would have very low capacity. Cryptate complexing of metal ions is a liquid-phase effect, and it may well be only a matter of time until large-scale processing is realized in this area. Possible limitations would be synthesis and cost of the cryptate systems. The liquid clathrates are quite new at this writing. They appear to possess high capacity and to avoid solid-state problems; whether the selectivities on which potential separations could be based are realizable is not known. An interesting property of liquid clathrate systems which is certainly unusual from a process point of view is the temperature dependence of stability: the clathrate $K[Al_2(CH_3)_6N_3] \cdot (benzene)_2.5$ forms at 70°C and dissociates on cooling. This is contrary to the usual behavior of clathrates which generally are dissociated by heat. Use of the liquid clathrate systems for separations depends on information regarding the capacity and selectivities in equilibrium with possible mixtures of aromatics, which is not available at present.

Normally then, clathration implies the process manipulation of solids. At this point in process design evolution, the temptation to simply scale-up laboratory precipitation-filtration-washing sequences to full-size industrial levels is encountered. As already indicated, the smaller volume product rates may permit such operations, but usually it will be found that large-scale solids handling (particularly over more than one equilibration) implies high costs in filtration or centrifugation equipment, large volumes of wash liquid implying high fractionation costs, and special solids transporting equipment.

A filtration system which has been carried through the pilot-plant stage is the separation of p-xylene and m-xylene by Werner salt clathration using $Ni(4\text{-methylpyridine})_4(SCN)_2$ [107, 108]. As proposed, the product is m-xylene with a reduced concentration of p-xylene. This can be accomplished in one clathrate precipitation stage, so the problems of multiple solid equilibration are avoided. The o-xylene and ethylbenzene isomers normally encountered in C₈ aromatic mixtures are largely removed from the process feed so good advantage can be taken of the high selectivity of the clathrate for p-xylene.

Numerous patents have been written on the use of solid clathrates in separation

processing [38]. An outstanding example of a successful approach has been the urea processing technique of Edeleanu GmbH. in industrial use

since 1955. Here the scheme utilizes filtration, but filtration made as operationally simple and inexpensive as possible [109]. Urea adduct is wetted by a polar aqueous phase and agglomerated into large lumps. Separation of adduct from the hydrocarbon phase is then accomplished by a coarse screen. The size of the aggregates is strongly shear-dependent: a high rate of stirring the adduct-hydrocarbon-water mixture produces very small lumps which will increase in size as the stirring rate decreases. Aggregation is a function of clathration conditions, crystal size, the liquid-phase properties, ratios of the phases, relative wettability of the solid by the two liquids, etc. Each clathration-agglomeration-screening sequence amounts to an equilibration. The high selectivity of urea and the process needs combine to reduce the number of equilibrations.

The processing of clathrates would be much more attractive if a way were found to move the solids countercurrently against the feed, over multiple stages of equilibration of solid with liquid. A favorable configuration for the use of clathrate solids which could be very inexpensive, at least in concept, is shown in Fig. 4. The host α -phase is brought into one end of a countercurrent contacting device, shown here as a column. The solid flows against a rising stream of feed mixture introduced at the bottom from which clathration removes the desired extract. The arrangement lends itself to multiple equilibrations of the same solid (staging) and is such as to require a lower inventory of host, produce purer products, and obtain higher recovery than a single equilibration could achieve [110]. The analogy with liquid-liquid contacting systems is evident, and can be extended to incorporate refluxing the clathrate flow against a stream of pure product, so that the extract in the clathrate phase is much purer than if clathrate

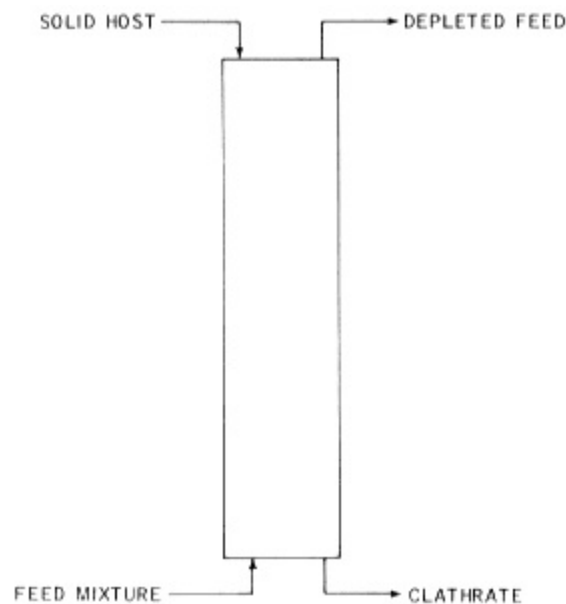


Fig. 4.
Countercurrent operation.

were equilibrated with the feed mixture (Fig. 5). Not shown in Figs. 4 and 5 are measures necessary to remove the extract from solid clathrate so that the α -phase can be returned to the contacting unit. If countercurrent operation is to provide more than a single equilibrium stage of clathration, the rate of the exchange reaction (16) must be sufficiently fast in relation to the residence time to allow equilibration of the clathrate with a varying succession of product concentrations, from the most dilute at the top of the tower to the most concentrated at the bottom. That experimental exchange rates are generally too low under conditions chosen for a separation scheme is only one reason for the fact that countercurrent clathration processes are not generally operational.

Movement of clathrate solids is inconvenient because the small particles tend to settle more slowly than larger ones, the solid fines tend to collect and plug lines, large surface areas of the solid phase imply large wash volumes to clean off depleted hydrocarbon phase, and there are normally two solid phases to move through the system (α -phase and clathrate) which may imply different flow properties. Between the maximum particle size allowable for clathration rate and the minimum size acceptable for flow, washing, or settling considerations, there may be a "gap." Even for solid-liquid systems where particle size control can be realized, moving solid beds are hard to implement. This can be seen in ion-exchange operations, for example, where the particle size is well defined. Some grinding of the resin beads by pumps can gradually produce fines and impair smooth operation.

One approach to these problems is to use fixed beds of solid. With a solid phase which does not cycle between α -phase and clathrate, this offers a partial solution to the difficulties. Plugflow of liquid past the particles can be achieved,

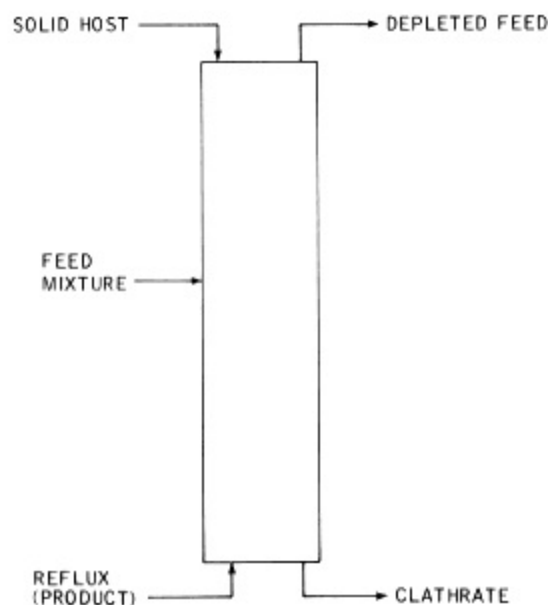


Fig. 5.
Countercurrent operation with reflux.

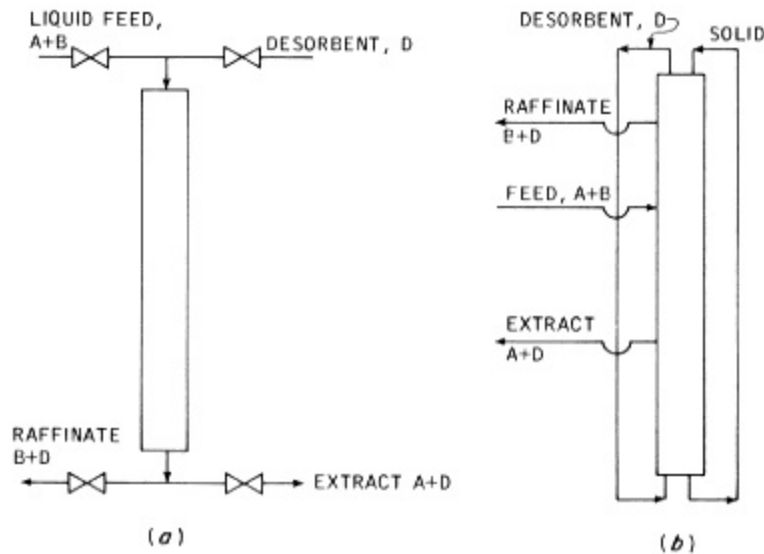


Fig. 6.
Adsorption schemes [111].
(a) Fixed bed, batch adsorption.
(b) Continuous adsorption.

which minimizes wash volumes in any configuration. The only flowing phase is liquid. Although fixed-bed operations are quite familiar for the use of solids, as in ion-exchange processes, drying of gases, some catalytic operations, and many molecular sieve separations, it should not be concluded that this is an optimal use of a solid reagent. Conventionally, the bed is first charged with an increment of feed mixture (loading). Then desorbent is added to elute the product. The procedure is a "batch" method. Broughton et al. have compared this to a continuous countercurrent use of solid. Figure 6 shows the two schemes [111]. As applied to the separation of a hypothetical binary liquid mixture, their analysis showed that continuous operation required 1/25 of the adsorbent inventory and about half the desorbent required for the batch system. In the present energy-intensive environment, where the adsorbent and desorbent requirements would be expected to reflect corresponding heat loads for the overall separation scheme, it is evident that a large driving force for solid continuous operations exists. To a large extent this need has been met by the "simulated moving bed" processes [111113]. A valving arrangement changes the liquid flow through a series of fixed beds in such a way that a given adsorbent increment is in contact with the same sequence of liquid compositions as if it were moving continuously through the scheme shown in Fig. 6(b). A large number of equilibrium stages of operation can be achieved in such a system. To date no such schemes have utilized clathrates as solid agents. An obvious problem would be the difficulty of maintaining a particle size regime which would allow high flow rates and multiple exchanges over cyclical changes in the solid crystal phase. If the exchange reaction (Eq. 16) is the only one, i.e., if the same clathrate phase prevails, control of particle size should be facilitated. Some of the technical difficulties of fixed-bed operations with clathrate systems

are being solved at the laboratory level. Kemula and Sybilska [114] first reported chromatographic use of the Werner salt clathrates. Operation depends on maintenance of the β -phase by setting limits on the lower levels of liquid guest concentrations to which the adsorbent is exposed, and by avoiding a second clathrate phase [69]. The β -phase $\text{Ni}(\text{4-methylpyridine})_4(\text{SCN})_2$ aromatic clathrates, for example, separated 1- and 2-methylnaphthalenes unless the methylnaphthalene concentration exceeded 0.1 M, in which case γ -phase clathrate appeared [115]. The guest exchange of interest was indicated to be that of naphthalenes for a combination of 4-methylpyridine and methanol in the clathrate. It has been found that use of these Werner salt clathrates in liquid chromatography can be strongly influenced by "auxiliary guests" such as m-xylene or 2,5-dimethylpyridine [116]. The separation involves kinetic as well as equilibrium effects, so more than simple cocrathration is involved. Detailed study of the kinetics of clathrate guest exchange in order to understand the mechanism is indicated. Although no large-scale process studies have appeared as yet, the chromatographic studies are making good progress. Economical processing would require optimization of the mobile liquid phase, the auxiliary guest, etc.

Gas chromatography utilizing Werner salt stationary phases has been demonstrated [117]. In this mode, the "permanent" empty β -phase lattice of the 4-methylpyridine systems produced a separation of p-xylene from m-xylene while the ethylpyridine and arylalkyl amine derivatives showed no such behavior. Also, substances not normally forming clathrates with the 4-methylpyridine salt hosts were separated at 70 to 80°C. Steps to prevent loss of 4-methylpyridine by volatilization in the carrier gas would be necessary on a long-term basis. A detailed study of the 4-methylpyridine β -phase was done by Allison and Barrer [80] who showed that it could be rapidly loaded with a wide variety of guest species, including rare gases, the chlorinated methanes, C_1 to C_6 n-paraffins, aromatics, cycloparaffins, isoparaffins, alcohols, CO_2 , CS_2 , and diethyl ether. Loading times varied from around 5 min to several days, slower rates being observed for more globular guest molecules such as isopentane, 2,2,4-trimethylpentane, or CCl_4 . Exchanges or sorptions from mixtures were not studied in this work, but the gas chromatography results indicate that mixtures can be treated successfully in a short time period. Gas chromatography studies are reported for tri-o-thymotide [118] and desoxycholic acid [119]. The promise of large-scale use of clathrates is considerably brightened by the β -phase studies so far reported. The requirement for a channel, rather than a cage, structure may limit the possibilities, as may the essentially metastable existence of the β -phase. Considerable experimental evidence indicating urea or thiourea β -phase properties exists, for example, in Refs. 102 and 120, but the $\beta \rightarrow \alpha$ phase transition apparently occurs so readily that a density determination of supposed β -phase urea in warm toluene indicated ordinary tetragonal urea [91]. McAdie and Frost [102] showed that the n-octane-urea clathrate, when decomposed under vacuum, produced tetragonal urea, as shown by X-ray diffraction. The external size and appearance of the decomposed crystal was not significantly different from the clathrate. This was explained

by the formation of microcrystals of tetragonal α -phase urea, left by the guest removal in a "fossil" of the clathrate. The particle size was much smaller than that of the

original α -phase, which could account for the fact that the pre-reacted urea rapidly formed adduct with guest vapors in the absence of a polar initiator. A clathrate β -phase, to provide processing viability as such, should be more stable than that of urea. The differences one might expect to find between an α -phase, an empty β -phase, and an α -phase "fossil" are presented in Table 3, which is meant only as a guide. Much more investigation of possible cases is needed; one can deduce that the alternate modifications resembling clathrate would be useful in solid-vapor operations, where a catastrophic change to the α -phase by dissolution-reprecipitation could be avoided.

Particularly in the case of relatively nonvolatile mixtures, the gas phase operations can be costly. Clathrate processing of liquids may not have the operational advantages of an empty β -phase, although in most cases this has yet to be conclusively demonstrated. In order to avoid the difficulties of preserving a possibly sensitive solid, most workers in the liquid separations area settle upon some way of using the α -phase of the host and minimizing its disadvantages (phase changes, solvent initiation, and slow rates). For example, urea has been used in a semicontinuous fixed-bed scheme by distributing it on a fiberglass support [121123]. Losses of urea from the fixed bed were held to the low amount of 10% per thousand cycles [121] because of the nature of the support and the random orientation of support fibers. That repeated cycling of the solid phase did not cause accumulation of fines and plug the bed was demonstrated in 2-, 6-, and 12-in. diameter beds. Polar solvent (methanol or propanol) was mixed with the feed hydrocarbon as a mutual host-guest solvent to achieve high rates. Process limitations were considered to be heat exchange on the clathration and declathration cycles and fractionation. The wash liquid necessary to remove adhering depleted feed mixture from the bed and the diluent required to declathrate the n-paraffin product both contribute to fractionation costs. Whether this interesting technology could be adapted to multiple staging and guest exchange is not reported. Possibly such adaptations could bring the scheme into competition with molecular sieve processing. Comparison factors would include the ease of product removal, the wash or

TABLE 3 Solid Modifications of Clathrate Host

Considerations	α -Phase	Empty β -Phase	α -Phase "Fossil"
X-ray pattern	Host	Clathrate	Host
Microscopic appearance	Host	Clathrate	Clathrate
Crystal size	Varied	Varied	Extremely small
Minimum guest activity	Kdissoc	?	Kdissoc
Polar solvent initiator	Necessary	Not necessary	Not necessary
Loading with "nonguest" (e.g., rare gases instead of aromatics in Werner salt clathrates)	No	Yes	No
Rates of loading	Slower, limited by Phase change	Rapid	Rapid
Effect of partial dissociation	None	Change to α -phase	Crystal growth

exchange liquid inventory, and the bed capacities. As in most urea processes which have achieved commercial status, the fixed-bed scheme does not require multiple equilibrations as designed; only a single "pass" utilizing the high selectivity available is used. Thus one filtration scheme [124] has operated commercially since 1967 for the single-stage extraction of n-paraffins from mineral oil.

For many years it has been evident that many operational difficulties in clathrate separations could be solved by manipulation of the solids as slurries which would be carried countercurrent to a hydrocarbon flow through a process [38, 94]. Slurry solvents have been proposed for such clathrate systems as urea, thiourea, and the Werner salt aromatic clathrates [11, 93, 125, 126]. Conceptually, the polar slurry solvent could serve to facilitate the separation of solid adduct from the hydrocarbon phase with which it is in equilibrium. A similar idea has been advanced to improve the separation of p-xylene from its isomers by crystallization [127]. In this case water (or an aqueous solution of ammonia or sodium hydroxide to adjust the density and freezing point) is mixed with the aromatic feed during p-xylene crystallization at 0°C. On centrifugation, the p-xylene crystals are physically separated from the depleted aromatic liquid phase by the water layer. As applied to urea clathrate operations, the polar liquid phase preferentially wets the solid, such that surface wettage by the hydrocarbon phase is reduced. The slurry technique is a way to avoid filters or centrifuges at each stage of clathration, since the critical separation of hydrocarbon from clathrate may be accomplished by simple decantation. For fast solid-hydrocarbon equilibration, however, some guest solubility in the slurry solvent is necessary or the polar liquid will simply isolate the kinetic advantage of high hydrocarbon solubility in the polar solvent against the loss in selectivity implied by solubility of nonclathrated substance (Fig. 7). The rates become critical when multistage operations are contemplated. The ratio of solid to solution can be varied within limits set by the selectivity and by flow considerations. It is desirable for the slurry to be thin enough to flow and be pumped through the process; otherwise the handling problems may be as severe as those of the solid itself. The extraction of feed components by the solution may introduce a desirable change in selectivity [93, 125]: if it is desired to simultaneously extract aromatics and n-paraffins from a hydrocarbon mixture, the urea slurry solvent can be chosen to extract aromatics. The second liquid phase introduces considerable versatility into the process design. Once the critical limitations on the separation are defined, a solvent may be selected to attach those limitations directly. Equilibration rate, selectivity, and capacity of the slurry will vary as a function of solvent. If a cocrystallator is needed to extend the clathrate stability range for recovery improvement, it may sometimes be chosen to selectively extract from the hydrocarbon phase into the slurry solution so as to simplify handling of the many process components [84]. Its introduction into the slurry solution phase in turn perturbs that phase and its effect on the separation.

The cocrystallator may act as an antisolvent and force the existence of a hydrocarbon phase in systems where the pure feed hydrocarbon is soluble in the slurry phase [83].

Over many equilibrations of the slurry from the recovery end of the separation to the product purification section, the hydrocarbon and host

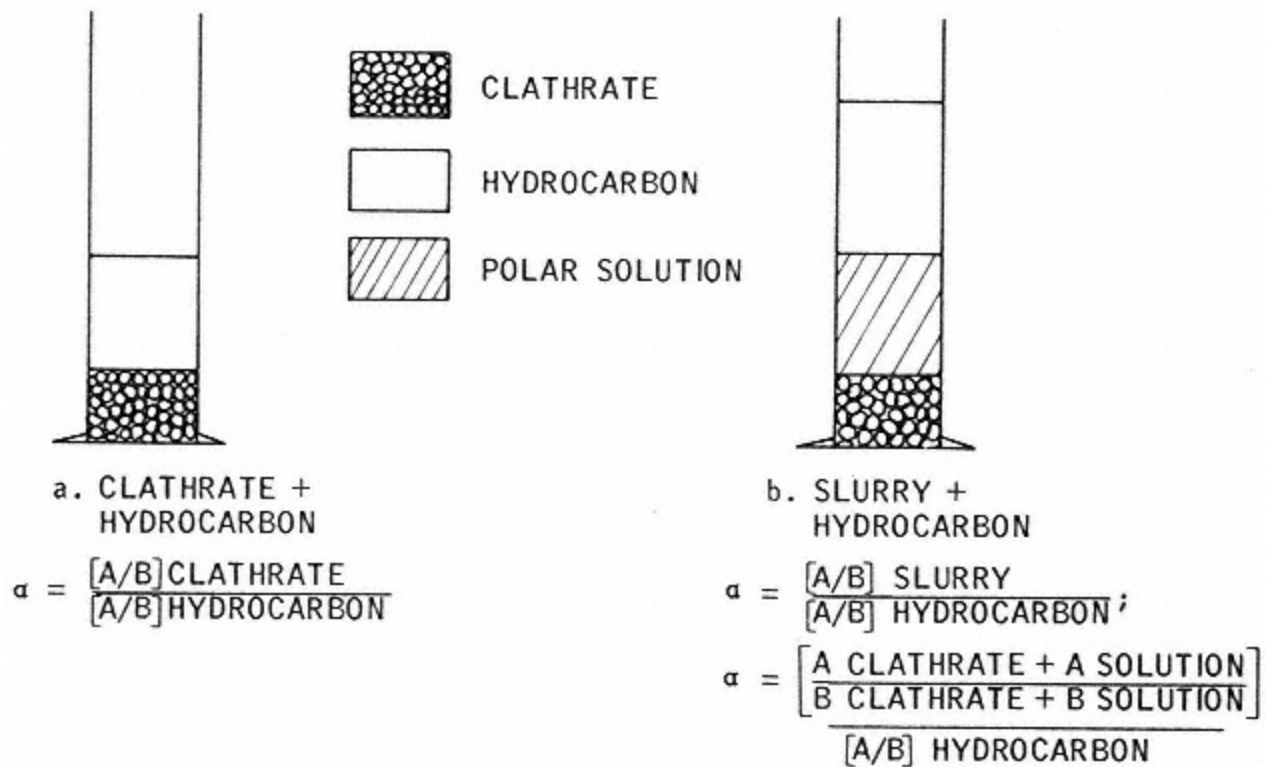


Fig. 7.
Operational selectivity.

solubilities in the solution may change markedly. Thus, if thiourea slurried in 2-methoxyethanol is used to extract benzene and cyclohexane from n-heptane (Fig. 8), the first stage at the top of the tower requires the equilibration of slurry initially containing no clathrate with rising hydrocarbon from which the equilibrations below have removed nearly all the extractable products. Heptane solubility in the solvent is very low and will be further reduced by a salting-out effect of dissolved thiourea [38]. The result is a minimum solubility of hydrocarbon in the solution. At the bottom of the tower (Stage 8), thiourea has been converted to the maximum loading of solid clathrate in the slurry, and is therefore at a minimum concentration in the solution phase. Hydrocarbon concentration is at a maximum in solution not only because of reduced dissolved thiourea but as a result of the fact that benzene and cyclohexane are fundamentally more soluble in the solvent than heptane.

Slurry operation, while conceptually avoiding many solids-handling problems, introduces a new set of constraints. The scheme is based on differences between the hydrocarbon mixture and the solid host or clathrate. The more nonpolar clathrate systems such as perhydrotriphenylene are molecularly so similar to many feed mixtures that it would be difficult to produce a slurry solution which would "carry" the clathrate and maintain a separate liquid phase in contact with hydrocarbon. (Note that pure solvent may be quite miscible with both feed liquid and host, yet produce an acceptable slurry system when

solvent, host, and guest are all present, because of salting out.) The formation of stable emulsions containing solid clathrate and both liquid phases is a common difficulty. Such an emulsion, if it moves with the slurry through the separation, will introduce a large amount of entrained hy-

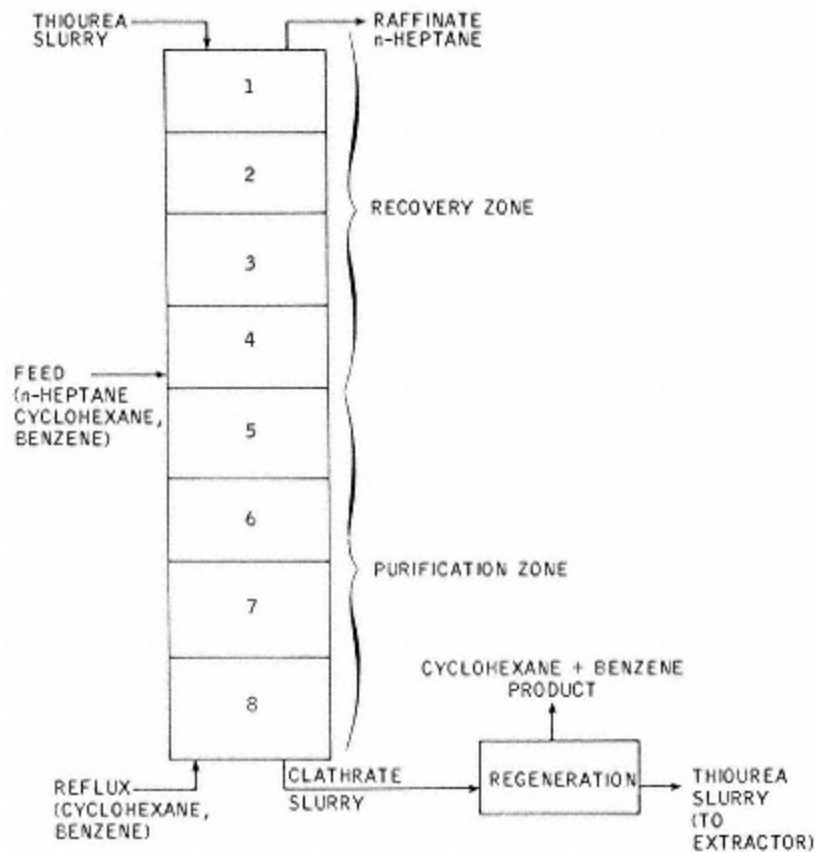


Fig. 8.
A schematic thiourea slurry extraction.

drocarbon phase which can drastically reduce the selectivity. If the emulsion tends to accumulate at the hydrocarbon-slurry interface, it will tend to plug the system quickly. The technology of handling such problems is not presently well defined. Some ingenious suggestions have been advanced for breaking up the emulsion and allowing a more complete phase split of hydrocarbon from slurry. Emulsion stability depends on such factors as temperature, phase ratios, relative wetting of the particles by the two liquid phases, densities, particle size, and shear. Thus mechanical vibration can destabilize a thixotropic mass of urea adduct, hydrocarbon, and alcohol-water solution [128]. Shear rate can be varied as the slurry moves through a separation, with intense mixing followed by gentle agitation to break the emulsion [129]. Addition of yet another phase can help: gas bubbling through the emulsion has been proposed [130]. The effect may be another form of mild agitation. If solid urea adduct particles are grown to a length of between 100 and 500 μm , the phase separation is reported to be greatly facilitated [131]. It may happen that emulsion formation is overcome by increasing the solubility of hydrocarbon in

the slurry solution. If this is done, a corresponding drop in slurry selectivity may result. Again, the use of large crystals to promote settling may bring on exchange rate problems.

The regeneration scheme (Fig. 8) can be any of a number of process options or a combination of more than one. The introduction of the solution phase does not generally rule out any of the usual methods (heat, dilution below the equilibrium limit, displacement by other guest, dissolution) of declathration employed for dry clathrates, and may even provide operational advantages. For example, the entire regeneration-product recovery operation can be accomplished by heating the product slurry and simple decantation if the host slurry solvent dissolves the host but not the guest [125]. A conveniently high temperature coefficient of host solubility may allow regeneration of the slurry at temperatures substantially lower than those required to dissociate dry clathrate.

One disadvantage of slurry operation is that probable solvents will possess at least some solubility in the hydrocarbon products, and generally will have to be recovered by finishing operations.

The guest exchange and cocrathration phenomena of clathrate systems can lead to unusual applications, not generally done on a large scale, but of interest in clathrate technology. Since urea clathrates increase in stability as the chain length of the guest molecule increases, it is natural to consider the clathration of high polymers such as polyethylene. The difficulty of getting host and guest species into solution in sufficient concentration to form clathrate made it difficult to make clathrates of any but the more soluble polymers, such as poly(ethylene oxide) [132] which was clathrated by urea from solution in benzene, or polyesters [133]. The exchange reaction has made it possible to clathrate polyethylene of molecular weight around 44,000. Urea clathrate of n-eicosane was heated to 120°C in xylene in the presence of dissolved polymer. The starting clathrate is unstable in xylene at 120°C, so the decomposition-reclathration sequence is more probable than a slower diffusional displacement. A cocrathration scheme for separation of small hydrocarbon molecules which normally do not form clathrate hydrates has been proposed [134]. The separation of straight-chain hydrocarbons from branched chains can be accomplished in hydrates stabilized by cocrathrating agents such as the halogenated methanes. Preferential clathration is shown for guests with smaller molecular "bulk" (i.e., n-butane > isopentane, 2,3-dimethylbutane > 2,2-dimethylbutane). Hydrate clathrates have cage, not channel structures. The generality of the cocrathration effect is well illustrated by this work since the hydrocarbon guests to be separated do not form hydrates in the absence of the halogenated methane.

Provided the clathrate cavity can accommodate reactants, intermediates, and products as guests, it would be expected that shape-selectivity effects over the course of a chemical reaction could be observed. Such has been the case, notably in the preparation of high molecular weight polymers from urea or thiourea clathrates [135]. It was concluded that only guest molecules which were partially overlapped in the initial clathrate channel were polymerized. Reaction was initiated by irradiation with high-energy electrons, and often

produced stereoregular polymers of unusually high molecular weight.

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Dehydrogenation

Dehydrogenation is a class of chemical reactions by means of which less saturated and more reactive compounds can be produced. There are many important conversion processes in which hydrogen is directly or indirectly removed. In principle, any compound containing hydrogen atoms can be dehydrogenated. But in this section only dehydrogenations of carbon compounds are treated, mainly those of hydrocarbons and alcohols. The largestscale dehydrogenations are those of hydrocarbons, and these are exemplified here in particular detail for the conversion of ethylbenzene to styrene, a very prominent current dehydrogenation process. Also prominent are conversions of paraffins to olefins, olefins to diolefins, cycloparaffins to aromatics, and alcohols to aldehydes or ketones.

Dehydrogenations of less specific character occur frequently in the refining and petrochemical industries, where many of the processes have names of their own. Some in which dehydrogenation plays a large part are pyrolysis, cracking, gasification by partial combustion, carbonization, and reforming. These

processes are described elsewhere in this handbook. Earlier reviews on dehydrogenation are those of Kearby [17] and Thomas [32].

In general, dehydrogenation reactions are difficult reactions. They require high temperatures for favorable equilibria as well as for adequate reaction velocities. Pure dehydrogenations are endothermic by 15 to 35 kcal/g-mol, and hence have large heat requirements. Active catalysts are usually necessary. Furthermore, since permissible hydrogen partial pressures are inadequate to prevent coke deposition, periodic regenerations are often necessary. Because of these problems with pure dehydrogenations, many efforts have been made to use oxidative dehydrogenations in which oxygen or another oxidizing agent combines with the hydrogen removed. This expedient has been successful with some reactions where it has served to overcome thermodynamic limitations and coke-formation problems.

The endothermic heat of pure dehydrogenation may be supplied through the walls of tubes (2 to 6 in.i.d.), by preheating the feeds, by adding hot diluents, by reheaters between stages, or by heat stored in periodically regenerated fixed or fluidized solid catalyst beds. Usually, fairly large temperature gradients will have to be tolerated, either from wall to center of tube, from inlet to outlet of bed, or from start to finish of a processing cycle between regenerations. The ideal profile of a constant temperature (or even a rising temperature) is seldom achieved in practice. In oxidative dehydrogenations the complementary problem of temperature rise because of exothermicity is encountered.

Other characteristic problems met in dehydrogenations are the needs for rapid heating and quenching to prevent side-reactions, the need for low pressure drops through catalyst beds, and the selection of reactor materials that can withstand the operating conditions.

Enthalpies and Equilibria

Table 1 shows enthalpies, in cal/g-mol, for some typical dehydrogenation reactions. The data are calculated at 800 K (527°C), mainly from American Petroleum Institute Project 44 data [27], but because the enthalpies change only slightly as the temperature is varied within the operating range, these numbers may be used to calculate adiabatic temperature changes or heat transfer requirements for the reactions. Tables of gaseous heat contents, or average values for gaseous heat capacities may be used for this purpose. It is apparent from Table 1 that the reactions become strongly exothermic when oxygen is added.

Equilibria can be readily calculated from free energies of formation (ΔG_f) or from $\log_{10} K_f$ in standard tables. The possible equilibrium conversions are essential guides in process design. As an example of a dehydrogenation equilibrium, calculated values for the dehydrogenation of propane are given in Table 2. This table illustrates the dominant effect of temperature on the equilibrium, as well as the very significant roles of pressure and of added diluents. Added hydrogen diluent, with the total pressure maintained at 1 atm abs, severely depresses the equilibrium conversion. Nevertheless, hydrogen is

sometimes added with the feed to diminish the rate of catalyst deactivation.

TABLE 1 Enthalpies of Reaction for Vapors at 800°K (527°C) (data from Ref. 27, except alcohols from Ref. 7)

Reaction	ΔH_{800} (cal/g-mol)
Ethane \rightarrow ethylene + H ₂	34,300
Propane \rightarrow propylene + H ₂	30,900
Butane \rightarrow 1-butene + H ₂	31,300
Butane \rightarrow t-2-butene + H ₂	28,500
n-Dodecane \rightarrow 1-dodecene + H ₂	31,200
1-Butene \rightarrow 1,3-butadiene + H ₂	28,400
t-2-Butene \rightarrow 1,3-butadiene + H ₂	31,100
1-Butene + 1/2O ₂ \rightarrow 1,3-butadiene + H ₂ O	-30,500
Methylcyclohexane \rightarrow toluene + 3H ₂	51,500
Methanol \rightarrow formaldehyde + H ₂	21,700
Methanol + 1/2O ₂ \rightarrow formaldehyde + H ₂	-37,200
Methanol + H ₂ O \rightarrow 3H ₂ + CO ₂	15,900
Isopropyl alcohol \rightarrow acetone + H ₂	14,200
Isopropyl alcohol + 1/2O ₂ \rightarrow acetone + H ₂ O	-44,700
Ethylbenzene \rightarrow styrene + H ₂	29,700

TABLE 2 Equilibrium Conversions in Percent for Propane \rightarrow Propylene + H₂

Temperature (°C)	1 atm, undiluted	1 atm, 10 mol inert	1 atm, 10 mol H ₂	2 atm, undiluted	10 atm, undiluted
427	6.35	19.0	0.45	4.49	2.0
527	24.6	56.5	7.0	17.7	8.0
627	59.8	87.5	37.1	46.6	23.0
727	87.0	96.5	76.5	78.0	36.2

Temperatures at which 50% dehydrogenation is possible at atmospheric pressure without added diluents are shown for several reactions in Table 3. Ethane requires quite a high temperature whereas isopropyl alcohol can be dehydrogenated at a rather low temperature if a sufficiently active catalyst is used. These temperature values serve as rough guides, but in design work it is necessary to make exact equilibrium calculations as illustrated by the examples that follow. In making these calculations, the tables of Noddings and Mullet [22] are very helpful. A limitation on the accuracy of such calculations, however, is imposed by uncertainties in the basic thermodynamic data, and it may well happen that experimental equilibrium results, based on careful sampling, analyses, and temperature measurements, will differ somewhat from calculated equilibria. But before such a conclusion is reached, it is essential that the equilibrium be approached from both directions, that sampling be carefully done, and that side reactions be minimal.

Equilibrium curves for the conversion of n-butane to n-butenes and butadiene at constant pressure are shown in Fig. 1. Here the butenes are an equilibrium mixture of 1-butene, trans-2-butene, and cis-2-butene, but the

TABLE 3 Temperatures at Which 50% Dehydrogenation Is Possible at Atmospheric Pressure with No Diluents Added

Reaction	Temperature (°C)
Ethane \rightarrow ethylene + H ₂	722
Propane \rightarrow propylene + H ₂	600
Isobutane \rightarrow isobutylene + H ₂	543
n-Dodecane \rightarrow 1-dodecene + H ₂	620
Ethylbenzene \rightarrow styrene + H ₂	621
t-2-Butene \rightarrow 1,3-butadiene + H ₂	656
Methanol \rightarrow formaldehyde + H ₂	411
Isopropyl alcohol \rightarrow acetone + H ₂	178

butadiene is solely 1,3-butadiene, since 1,2-butadiene can only form in very small amounts. An inert diluent (steam or nitrogen, for example) increases possible conversions to olefins and dienes at a given temperature. A reduced pressure could also be used for this purpose, with nearly equivalent results at the lower conversions and even more effect at higher conversions.

Equilibrium calculations for the conversion of ethylbenzene to styrene in a constant pressure flow-system will be given here in greater detail. The process is carried out with an added inert diluent, normally steam. The reaction is written

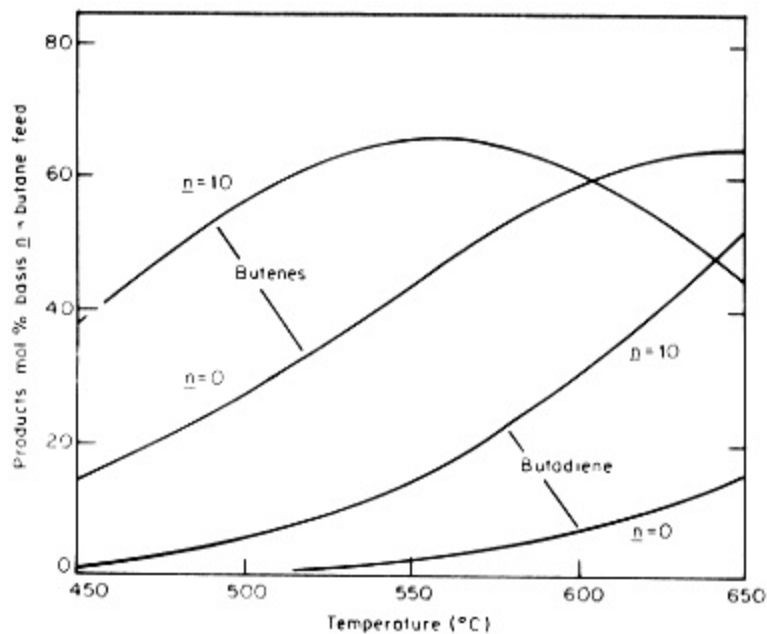
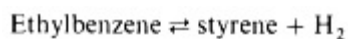


Fig. 1.

Equilibrium in the system $n\text{-butane} \rightleftharpoons n\text{-butenes} \rightleftharpoons 1,3\text{-butadiene}$ 1 atm with n moles inert per mole total C₄.

The equilibrium constant is $K_p = (P_H)(P_S)/(P_E)$, where the P's are partial pressures in atmospheres absolute. In the general case there will be n moles of steam per mole of ethylbenzene initially present, and n can be taken as a constant since the consumption of steam by reaction to form H_2 and CO_2 is small. However, the side reactions become significant in the case of hydrogen, and somewhat more than 1 mol of H_2 is formed per mole of styrene, say a mol/mol. Thus, if the fractional conversion of ethylbenzene at equilibrium is x , the partial pressures at equilibrium will be

$$P_E = (1 - x)P/(1 + n + ax)$$

$$P_S = xP/(1 + n + ax)$$

$$P_H = axP/(1 + n + ax)$$

Then the conversion at the temperature and pressure of the reactor exit cannot exceed that given by

$$K_p = ax^2P/(1 - x)(1 + n + ax)$$

where $\ln(K_p) = -\Delta G/RT$, P is in atmospheres absolute, ΔG is the standard free energy change in cal/g-mol, $R = 1.987$ cal/g-mol $^{\circ}K$, and T is in $^{\circ}K$. From the tables of American Petroleum Institute Project 44 [27], the following values of K_p are obtained:

Temperature, $^{\circ}C$	427	527	627	727
K_p , atm	0.00329	0.0469	0.376	2.00

Using these numbers and the interpolated data, the curves of Fig. 2 have been calculated. A value of $a = 1.3$ at $x = 0.4$ is reasonable from the data of Wenner and Dybdal [35]. The calculated equilibria are in fairly good agreement with experimental data, though there are some data indicating that true equilibrium may be at a little lower conversion than calculated from the thermodynamic data. In practice, a high temperature, a low pressure, and dilution with an inert material (steam, etc.) are used to favor a high equilibrium conversion.

Design Principles

Selection of operating conditions for a straight dehydrogenation reaction often requires a compromise. The temperature must be high enough for a favorable equilibrium and for a good reaction rate, but not so high as to cause excessive cracking or catalyst deactivation. The rate of dehydrogenation reactions diminishes as conversion increases, not only because equilibrium is approached

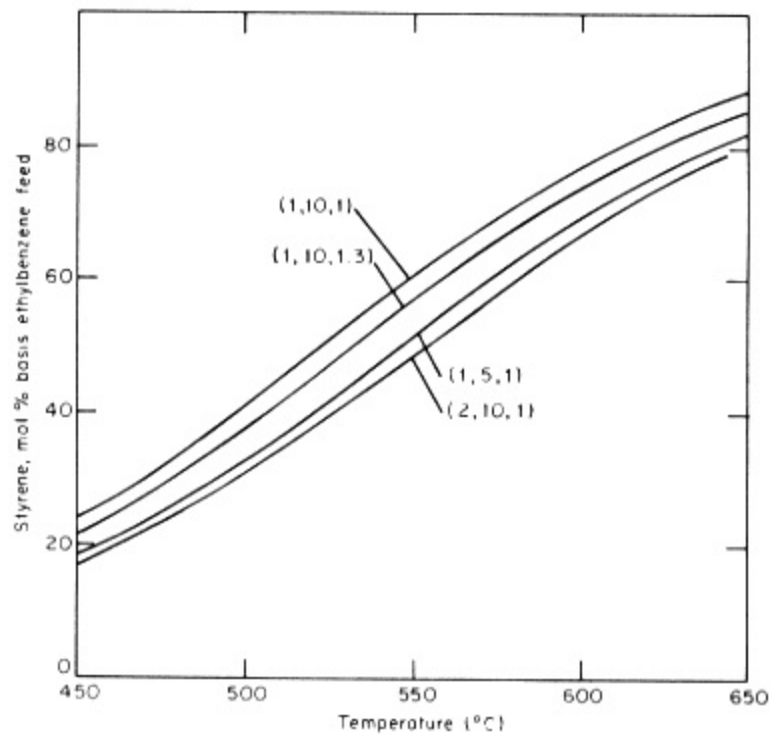


Fig. 2.

Equilibrium for ethylbenzene \rightleftharpoons styrene. Parentheses show (P, n, a) where P is in atmospheres, n is moles inert diluent, and a is moles H₂ formed per mole styrene.

more closely, but also because in many cases reaction products act as inhibitors. The ideal temperature profile in a reactor would probably show an increase with distance, but practically attainable profiles normally are either flat or show a decline. Large adiabatic beds in which the decline is steep are often used.

The reactor pressure should be as low as possible without excessive recycle costs or equipment size. Usually it is near atmospheric, though reduced pressures have been used in the Houdry butane dehydrogenation process. In any case, the catalyst bed must be designed for a low pressure drop.

Rapid preheating of the feed is desirable to minimize cracking. Usually this is done by mixing prewarmed feed with superheated diluent just as the two streams enter the reactor. Rapid cooling or quenching at the exit of the reactor is usually necessary to prevent condensation reactions of the olefinic products. Materials of construction must be resistant to attack by hydrogen, capable of prolonged operation at high temperature, and not be unduly active for conversion of hydrocarbons to carbon. Alloy steels containing chromium are usually favored. Steels containing nickel are also used, but they can cause trouble from carbon formation. If steam is not present, traces of sulfur compounds may be needed to avoid carbonization. Both steam and sulfur compounds act to keep metal walls in a passive condition.

Dehydrogenation Processes of Industrial Importance

Ethane → Ethylene

This reaction is currently effected by pyrolysis (no catalyst), using temperatures of 800 to 900°C and steam diluent at moderate pressures of 2 to 5 atm. The selectivity to ethylene is 85 to 90%. Externally heated pyrolysis tubes are used. Details of this process are given elsewhere in this work.

Propane → Propylene

The reaction can be carried out catalytically using a chromia-alumina catalyst at about 550 to 600°C. A kinetic study of this reaction over a potassiumpromoted chromia-alumina catalyst was made by Suzuki and Kanero [31]. In commercial practice it is more usual to pyrolyze propane to obtain a mixture of ethylene and propylene.

n-Butane → n-Butenes → Butadiene

This process has been much used to obtain butenes and butadiene. A chromia-alumina catalyst is used at 550 to 600°C [17, 32]. For butenes production, operation at atmospheric pressure is acceptable, but when butadiene is the main product it is preferable to operate at a reduced pressure of about one-fourth of an atmosphere. In the most prominent process for this reaction, the Houdry Process [14], the catalyst bed is diluted with inert solids which act as heat carriers, receiving heat during the regeneration periods when coke is burned off with air, and supplying heat for the endothermic reaction during process periods of 7 to 50 min duration. A process period of 15 min may be normal. A study of the kinetics of reaction, coking of catalyst, and reactor design for low-pressure dehydrogenation of 1-butene to butadiene over chromia-alumina catalyst was published by Dumez and Froment [10]. An earlier kinetic study of butane dehydrogenation, primarily to butenes, and using chromia-alumina catalyst at 1.1 to 2.7 atm pressure with 30 min process periods was that of Dodd and Watson [9]. Conversions in this process are limited to 40% or less by equilibrium.

n-Butenes → Butadiene

There are three general methods of converting n-butenes to 1,3-butadiene. The first is the Houdry process, just mentioned, in which dehydrogenation is at reduced pressure for brief process periods over a chromia-alumina catalyst. In this process the feed can be butenes, butane, or a mixture.

Second is the continuous dehydrogenation in the presence of steam over a suitable catalyst at atmospheric pressure and about 620°C. This process has been widely used, with the butenes usually coming from refinery cracking processes. Initially the Esso 1707 catalyst based on MgO was used [17] and

hourly steam regenerations were needed. An excellent study of the kinetics for this system was published by Beckberger and Watson [4]. Later, catalysts based on iron oxide were introduced, and these permitted dehydrogenation with no or very infrequent regenerations. The Shell 205 catalyst (62.5% Fe_2O_3 , 2.2% Cr_2O_3 , and 35.3% K_2CO_3) is a prominent example. With it, about 12 mol of steam are used per mole of butenes. At a conversion of 30%, the selectivity to butadiene is 75 to 80% mol. The steam serves to carry heat, to lower the hydrocarbon partial pressure, and to maintain the catalyst in an active condition. The steam is preheated to a higher temperature than the butenes stream, the two are mixed immediately before entering the large adiabatic catalyst bed, and at the exit from the bed the products are rapidly cooled by water quench or by tubular heat exchangers. Typical operating conditions are 590 to 650°C, butenes gas hourly space velocity (for gas at NTP) 200 to 600, $\text{H}_2\text{O}/\text{C}_4\text{H}_8$ 8 to 14, conversion per pass 25 to 35%, and selectivity 70 to 80%. A 3/16 in. diameter catalyst pellet is normally used, but as Voge and Morgan [34] have shown, selectivity is somewhat improved with smaller sizes in the laboratory tests. However, in commercial plants the size may have a critical effect on pressure drop and bed integrity.

Another catalyst that has been used for butenes dehydrogenation in the presence of steam is the Dow Type B, which consists of calcium and nickel phosphates promoted with a small amount of chromium oxide [23]. This catalyst gives a higher selectivity to butadiene of about 90%, but requires more steam (20 mol per mole of butenes) and also requires hourly regeneration with air.

The third method of butenes dehydrogenation is oxidative dehydrogenation over a catalyst by means of added air. This has the great advantage of not being limited by equilibrium. The reaction is highly exothermic but it can be operated adiabatically if a sufficient quantity of inert gases is present. Oxidative dehydrogenation has been developed for commercial operation by Phillips as the O-X-D Process [15, 16]. Air and steam are mixed, heated, and mixed with butenes feed. The mixture is passed over the oxidative dehydrogenation catalyst in an adiabatic reactor at about 480 to 590°C. The butenes gas hourly space velocity is in the range 200 to 600, $\text{O}_2/\text{C}_4\text{H}_8$ is about 1, $\text{H}_2\text{O}/\text{C}_4\text{H}_8$ about 35, temperature rise about 100°C, conversion of butenes 70 to 80%, and selectivity 85 to 90%. Suitable catalysts for this reaction may be of the bismuth-molybdenum oxide type, or of the tin phosphate type, or still others. Variants of the oxidative dehydrogenation process have also been developed by British Petroleum [20] and by Petro-Tex [3]. There has been much recent research effort in the field of oxidative dehydrogenation, and various papers describe studies of catalysts for butenes conversion by this method [13, 26]. A kinetic study of the oxidative dehydrogenation of butenes to butadiene over ferrite catalyst was described by Sterrett and McIlvried [30].

Higher Paraffins to Olefins

Paraffins from about C_6H_{14} to about $\text{C}_{20}\text{H}_{42}$, usually segregated into four-carbon fractions, can be dehydrogenated to monoolefins at low pressure over

nonacidic noble metal catalysts. A mixture of n-olefins is obtained since the position of the double bond shifts readily under dehydrogenation conditions. This multiplicity of olefins on the right-hand side of the chemical equation raises the equilibrium conversion relative to what it would be with only a single olefin formed. An example of such a process is the PACOL Process of UOP, which is used to prepare detergent range olefins for alkylation from n-paraffins [5, 33]. Conversion levels are of the order of 20 to 40%, and selectivity to monoolefins is about 90%. Diolefins, cracked products, and aromatics are undesired minor by-products, produced at selectivities of 2 to 4% each (basis feed molecules converted). A separation process is necessary to isolate unconverted n-paraffins for recycle to the dehydrogenation step. Selective extraction of olefins or olefin alkylation followed by distillation serves for this separation. A fixed bed of catalyst is used in which the reaction is carried out in the vapor phase in the presence of excess hydrogen. Little detail has been published.

Paraffins → Olefins, General

The lower paraffins can be dehydrogenated over chromia-alumina or over noble metal catalysts. For higher paraffins only certain noble metal catalysts can be used since formation of aromatic rings is prominent for six or more carbon atoms with a chromia-alumina catalyst. Paraffins cannot be dehydrogenated at practical conversions over the alkalized iron oxide catalysts in the presence of steam, nor can they be dehydrogenated by the oxidative processes used for butenes conversion. There has been much research interest devoted to finding an oxidative dehydrogenation process suitable for paraffins. Good conversions are possible by use of iodine or sulfur compounds as initiators [12, 18, 25]. Iodine is especially effective as a dehydrogenating agent, and when used in conjunction with an alkaline acceptor to bind the HI produced can give very extensive dehydrogenation to olefins, diolefins, or aromatics. By reaction with oxygen, the iodine can then be regenerated from the acceptor-HI combination [18]. Operating conditions for this process are quite corrosive, construction costs are high, and iodine losses must be very low.

Other promoted oxidative processes for paraffins use catalysts and smaller amounts of iodine or sulfur compounds along with added oxygen. There is much continuing research on various types of oxidative dehydrogenation, including treatment in the presence of oxygen and small amounts of halides over various catalysts [3], and treatment in the presence of oxygen and hydrogen sulfide over suitable catalysts [12]. An older review article on oxidative dehydrogenation of hydrocarbons lists 177 references [28].

Cyclohexanes → Aromatics

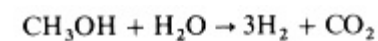
This is one of the easier dehydrogenations. Equilibrium conversion is greater than 80% above about 350°C, even at a pressure of 5 atm. Platinum-alumina catalysts are very effective, and this is one of the more important reactions in the

platinum catalyst reforming of gasoline for octane improvement. In fact, the reaction is not usually carried out as a simple reaction of a single cyclohexane, but instead the desired aromatics are recovered from the mixed products of reforming. For details see the section on reforming, or the book of Thomas [32].

Alcohol → Aldehyde or Ketone

A typical reaction is that of isopropyl alcohol to give acetone and hydrogen. The equilibrium is favorable at temperatures of 250°C or above, but somewhat higher temperatures are needed for a good rate. Catalysts that can cause dehydration have to be avoided. Metallic copper is effective, and may be used on an inert support or as particles of brass. Supported silver is another suitable catalyst. Certain oxide catalysts, such as copper chromite, can be used. Conditions are 300 to 450°C, 1 to 5 atm pressure, and 1 to 5 LHSV. Externally heated tubes are used to avoid large temperature decline. Alternatively, an oxidative dehydrogenation with air added and partial conversion to both steam and hydrogen may be effected using silver on an inert support.

Conversion of methanol to formaldehyde is usually done oxidatively over silver catalyst or over an iron-molybdenum oxide catalyst [32]. A special type of dehydrogenation, represented by the reaction



can be used to convert methanol to hydrogen. Manganous oxide on silica gel is a very active catalyst which operates in a water-methanol solution under pressure at about 130°C.

Ethylbenzene → Styrene

Styrene is manufactured on a very large scale for use in various polymers. Most of the styrene is made by dehydrogenation. The technology has been continually improved and has reached an advanced status. Design needs include: (1) a high temperature and a low pressure for favorable rate and equilibrium, (2) an active and selective catalyst, (3) a method of supplying the heat of reaction, (4) the avoidance of side reactions, (5) a low pressure drop through the catalyst bed, (6) the highest possible conversion to avoid costly recycle, (7) reactor materials suitable for operating conditions, (8) conservation of heat and steam, and (9) good stream factor. These needs have been adequately met. For example, large plants have demonstrated uninterrupted operation for over 18 months.

There are several competing processes, but all appear to use iron oxide catalysts and steam dilution. Prominent are: (1) Monsanto-Combustion Engineering-Lummus [1, 8], (2) Union Carbide-Cosden-Badger [2], and (3) Societe Chimique des Charbonnages [29]. Proprietary styrene processes are operated by Dow Chemical Co. and by BASF AG.

Reactors for ethylbenzene dehydrogenation usually contain large adiabatic beds of catalyst. Vapor flow is either downward or radial-outflow. Beds may be staged, with intermediate heaters or intermediate addition of hot gases to supply the heat of reaction in part. By means of such devices and possibly other undisclosed innovative reactor designs, it has been possible to increase operating conversion levels from about 40% to about 60%, with consequent savings. German practice (BASF) has been to use catalyst in externally heated tubes, a lower steam dilution, and a conversion level of about 40% [24].

In the adiabatic reactors the pressure is not much above 1 atm abs, and the pressure drop through the reactor must be kept low. Since the inlet temperatures border on those for thermal cracking of ethylbenzene, the inlet residence time must be kept low. Usually highly superheated steam is mixed at the reactor entrance with ethylbenzene vapors which are somewhat below the desired inlet temperature. Operating conditions in the catalyst beds may cover the following ranges:

Temperature	550 to 650°C
Pressure	0.7 to 3 atm abs
Inerts/hydrocarbon	10 to 20 (inerts, mainly steam)
Flow rate of ethylbenzene	0.3 to 1.5 vol./vol. catalyst h
Conversion, %	40 to 65
Selectivity, %	85 to 95 mol styrene/mol ethylbenzene converted

Catalysts for ethylbenzene dehydrogenation have undergone a continuing evolution. The earliest catalyst was bauxite (an impure aluminum oxide). This was replaced in the United States during the mid-1940s by catalysts based on MgO and Fe₂O₃ [17]. Early European history was reviewed by Ohlinger and Stadelmann [24], starting with I. G. Farben studies and continuing with the postwar work of BASF. The best BASF catalyst as of 1965 was Lu-144F, with the composition 85% Fe₂O₃, 7.7% ZnO, 0.7% Al₂O₃, 0.5% CaO, 0.5% MgO, 5% KOH, 0.3% K₂CrO₄, and 0.3% K₂SO₄. However, in most of the world the Shell 105 catalyst became the standard. This catalyst consists of 87.9% Fe₂O₃, 2.5% Cr₂O₃, and 9.6% K₂O. In use, the red Fe₂O₃ is largely converted to black Fe₃O₄ which is magnetic and electrically conductive, while the K₂O is partially converted to K₂CO₃. Lee [19] gives much information about composition and effectiveness of iron oxide catalysts for styrene manufacture, including X-ray data for fresh and used Shell 105. He notes that these catalysts are readily poisoned by chlorides.

Catalysts are used as 1/8 in. diameter cylindrical pellets or sometimes as larger particles. The effect of particle size on selectivity for the related Shell 205 catalyst was noted in butenes dehydrogenation [34]. The effect is less in the styrene reaction, and the increased pressure drop with smaller particles may very well cancel any gain in intrinsic selectivity.

The velocity of the dehydrogenation reaction is determined by catalyst activity, temperature, vapor composition, and pressure. In adiabatic reactors, equilibrium is closely approached at the outlet, and the distance from equilibrium may govern the reaction velocity. An early kinetic analysis of

reactor design for ethylbenzene dehydrogenation in externally heated tubes and in adiabatic beds was that of Wenner and Dybdal of Monsanto [35]. They give integral conversion data with 3/16 in. pellets of a catalyst similar to Shell 105 (their catalyst "B"). Later differential and integral reactor studies with 10 to 30 mesh granules of Shell 105 were reported by Carrà and Forni [6]. The reaction rate was essentially independent of ethylbenzene partial pressure at low conversions, but was strongly inhibited by styrene. Rate data are well fitted by the equations

$$dx/d(W/F) = k_1(P_E - P_H P_S / K) / (P_E + b P_S)$$

$$dy/d(W/F) = k_2 P_E / (P_E + b P_S)$$

where x is the fractional conversion to styrene, y is the fractional conversion of ethylbenzene to the by-products benzene and toluene, W is catalyst weight, F is inlet flow rate of ethylbenzene, the k's are reaction velocity constants, K is the equilibrium constant, the P's are partial pressures, and b is an adsorption constant, evaluated to be 8.0. An additional small term can be added to the denominator to account for rates at higher pressures, which were extended to 11 atm in the work of Carrà and Forni. These equations are based on presumption of a parallel reaction to form the by-products. However, selectivity to styrene does decline at high conversions, probably in part from the reaction of styrene with steam to form CO₂, toluene, and other products. To account for this, a term $-k_3 P_S$ should be entered at the right of the first equation, and a term $+k_3 P_S$ should be entered at the right of the second equation. An indication of the effect of conversion on selectivity is given by the following data:

Conversion of ethylbenzene, %	10	25	40	Refs.
Selectivity to styrene, %	97.5	93.5	90	35
H ₂ /styrene in product	1.1	1.25	1.4	35
Selectivity to styrene, %	96.7	95.4	92.8	24

The exact selectivity (defined as moles of styrene obtained per mole of ethylbenzene converted) is, of course, somewhat dependent on plant design, pressure, temperature, catalyst, and steam dilution as well as on conversion level.

Since a number of different reactions are involved, including dehydrogenation, cracking to ethylene and benzene, hydrocracking to toluene and methane, and reaction with steam to produce hydrogen and CO₂, there should be an optimum temperature profile in the reactor for maximum selectivity to styrene. This problem was conditionally treated by Modell [21], but a lack of well-established values for the activation energies of the various reactions prevented firm conclusions.

Alternative methods of dehydrogenation of ethylbenzene to styrene have been studied.

Oxidative dehydrogenation using oxygen as a reactant is not as successful as in the case of butenes conversion to butadiene [26]. However, SO₂ as an oxidant with proper catalysts gives high conversion and selectivity to

styrene [11, 26]. Small amounts of sulfur-containing heterocycles are byproducts. In the experiments of Gaspar and co-workers [11], SO_2 and O_2 were used in conjunction, the O_2 being added in three successive increments in a flow system. Using mole ratios of $\text{SO}_2/\text{ethylbenzene} = 0.15$, total $\text{O}_2/\text{ethylbenzene} = 0.45$, $\text{H}_2\text{O}/\text{ethylbenzene} = 4$, and an alkalized alumina or titania catalyst at 635°C , 85% conversion was obtained with a selectivity to styrene of 94%.

Industrial Processes

A process developed jointly by Monsanto and the C-E Lummus division of Combustion Engineering, Inc., is offered for licensing. A styrene plant of this design with capacity of 670,000 t of styrene per year has been built at Texas City and is said to be the largest in the world. The dehydrogenation of ethylbenzene is carried out in the vapor phase in an innovative reactor design that has permitted extremely large single-train units to be built. The commercially available catalyst is replaced about every 2 years. Starting from ethylene and benzene, the net requirements per kilogram of styrene are 0.307 kg ethylene, 0.820 kg benzene, 1.4 kg of 75 lb/in.² gauge steam, 0.088 kWh electricity, and 1545 kcal fuel. Conversion is probably about 60% with a selectivity of the order of 90%. Catalyst and chemicals cost about 0.2¢/kg of styrene [1,8].

Another integrated process, developed by Carbide-Cosden-Badger, has likewise been used for quite large units [2]. Dehydrogenation is again in the vapor phase with steam (and perhaps other) diluent. This process is said to use unique methods to improve the dehydrogenation step without adversely affecting catalyst performance or life. Conversion, selectivity, and amount of

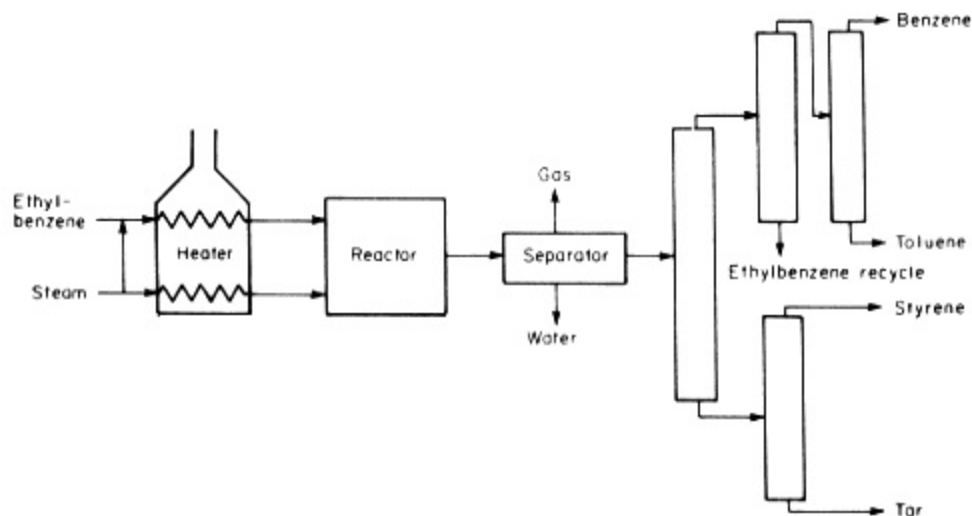


Fig. 3.
Generalized flow diagram for ethylbenzene dehydrogenation.

steam are variables that must be optimized in each design. One plant using this process has completed 19 months of continuous operation, and a single charge of catalyst lasted for 27.5 months of operation, giving over 3000 kg styrene/kg catalyst.

A generalized flow diagram for styrene production by dehydrogenation in an adiabatic catalyst bed is shown in Fig. 3. Variations are possible in the sequence of distillation columns as well as in the design of the reactor itself.

Other styrene processes have been developed by Dow Chemical, by BASF (Badische) in Germany, and by Société Chimique de Charbonnages in France. Little has been published about the Dow process. BASF has used semiisothermal reactors with the catalyst contained in externally heated tubes that are about 16 cm diameter by 300 cm long [24]. Since heat is supplied through the tube walls, it is possible to operate with lower steam dilution in the BASF process, and consequently the more expensive reactor is offset by lower steam expense. The French company offers its process for licensing. It is said to employ a multistage dehydrogenation reactor to obtain high conversion [29].

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Deionization

W. F. McIlhenny

The presence of dissolved materials in commercial and industrial waters is undesirable because these materials are often the cause of processing and product problems. Corrosion, foaming, generation of taste and odor, staining and adulteration of commercial products, undesirable effects on human health, and the formation of precipitates as scale in heat exchange equipment and in steam generators can all be caused by dissolved materials [3].

Perhaps the most troublesome set of dissolved constituents is those formed by the

dissociation into ions of a chemical compound dissolved in a water solution. All terrestrial, naturally occurring waters contain dissolved ionizable materials at various levels of concentration. If the concentration is extremely low, the water is termed "deionized" even though determinable levels of ionic materials remain. "Fresh water" contains relatively low concentrations, and "brackish waters," "saline waters," and "brines" contain increasing amounts of electrolytes. At least 95% of the total content of dissolved solids of almost every natural water is comprised of some combination of only eight ions:

Sodium (Na^+)
 Potassium (K^+)
 Calcium (Ca^{2+})
 Magnesium (Mg^{2+})
 Chloride (Cl^-)
 Bicarbonate (HCO_3^-)
 Sulfate (SO_4^{2-})
 Carbonate (CO_3^{2-})

The only chemical requirements restricting the possible number of variations are that the cation equivalents be equivalent to the anionic equivalents and that the solubility product constant of any possible compound not be exceeded. Many other ionic constituents are found in natural waters and in industrial and commercial solutions, but generally at a low level. It is the eight major ions that determine the chemistry, effects, and technology of water ion management; and it is the removal of these eight ions with which any process for desalting, demineralization, or deionization must contend.

Although the separation of water or ions from an electrolytic solution for the purpose of obtaining a water solution with a lesser ionic content is always a deionization process, the term "deionization" is usually reserved for the production of very pure, very high quality water. "Desalting" is the term usually used when ions are removed to produce a usable solution with a somewhat higher content of dissolved solids.

The quality of the product water, and often of the demineralizing or desalting process, is often determined by the end use. Because dissolved electrolytes allow conductance of an electric current, electrical conductivity, usually measured in reciprocal resistance units, micromhos per centimeter ($\mu\text{mho}/\text{cm}$), is a measure of water purity. High purity results in low conductivity. Weakly ionized components, such as hydrated silica, contribute only slightly to the electrical conductivity of a water solution.

Some quality requirements for various industrial waters are shown in Table 1. The preparation of the highest quality waters as required by high-pressure boilers and nuclear plant steam systems requires the most exacting water treatment, and also often requires subsequent ion control internally in the water systems.

Other water uses, both industrial and municipal, do not require as high a quality of water. Desalting is therefore usually designed for the removal of only sufficient dissolved electrolytes to make the remaining solution usable for the required purpose. A level of 500 mg/l is used by the World Health Organization as a permissible standard for potable water supplies, with specific limits for certain other constituents.

Desalting

In all desalting, deionization, and demineralization processes, energy must be expended to separate a less saline from a more saline solution. The minimum

TABLE 1 Selected Water Quality Tolerances and Ion-Exchange System Capabilities

Industrial Use	Total Solids (mg/l)	Conductivity (mho/cm)	Refs.
Water Quality Tolerances			
Boiler waters (lb/in.2gauge):			
0 to 300	3500		3
450 to 600	2500		3
901 to 1000	1250		3
1000 to 2000	500		3
Boiler feedwater	50		9
over 400 lb/in.2gauge			
Potable water	500		17
Confectionary	50100		9
Viscose rayon	100		9
Reagent grade water,	0.1	0.06	2
Type I			
Nuclear feedwater:			
Pressurized water	50 ppb		13
Boiling water		0.06	2
Ion Exchange System Capabilities			
Reverse osmosis		55	14
Single distilled water		20	4
(in glass)			
Two-bed deionizer	23	1015	5
Triple distilled water		1.0	4
(in glass)			
Four-bed deionizer	0.21	15	1
Reverse osmosis + mixed		0.1	14
bed			
Mixed bed	0.20.5	0.51.25	1

energy requirement, for example, for removing salt from seawater of salinity 34.3 parts per thousand at 25°C is 0.70 kWhm⁻³ (2.65 kWh/1000 gal). This minimum energy requirement increases as the amount of water removed from the solution increases and also increases with increasing temperature. In actual practice it is, of course, impossible to obtain minimum energy requirements, and about four times the thermodynamic minimus is about the best that can be attained [15].

In any process for desalting, demineralization, or deionization, the separation of ions and water depends upon differentiation of both into two phases or segregation into two solutions separated by a semipermeable barrier. A convenient classification of deionization or desalting processes based on removal of salts or water, of the segregated phase, and the form of energy supplied is shown in Fig. 1. Usable water can be produced by either removal of the dissolved salts or by the removal of water from the original saline solution [10]. The primary form in which energy is supplied for each of the processes is

shown. Hybrid processes using a combination of these simpler processes have been proposed but have not been extensively investigated.

Examination of Fig. 1 shows that all processes for the deionization of a water solution require that either a phase change occurs or that a diffusion of water relative to the dissolved salts occurs, and that in either case transport of water must be made against a finite resistance. Transfer occurs under the action of a potential driving force against a resistance. The driving force is temperature difference, for example, for both distillation and freezing, electrical potential for electrodialysis, pressure difference for reverse osmosis, and electrolyte concentration for ion exchange. In general, a good deionization process uses a low-grade energy source, and the transfer takes place through an inexpensive, low-resistance surface or uses a phase change requiring minimum energy. No process completely satisfies all of these requirements.

In general, where water is separated by a phase change such as in distillation or reverse osmosis, salt transport is not involved and high-quality water is produced whether required by the usage or not. In those processes where salt is transported, such as electrodialysis or ion exchange, more control of the quality of the water product is possible.

There are three principal deionization processes used for the preparation of high-quality, low-conductivity water: distillation, reverse osmosis, and ion exchange. The relative ability of these processes to produce high-quality water is also shown in Table 1. For the highest quality, these processes may be

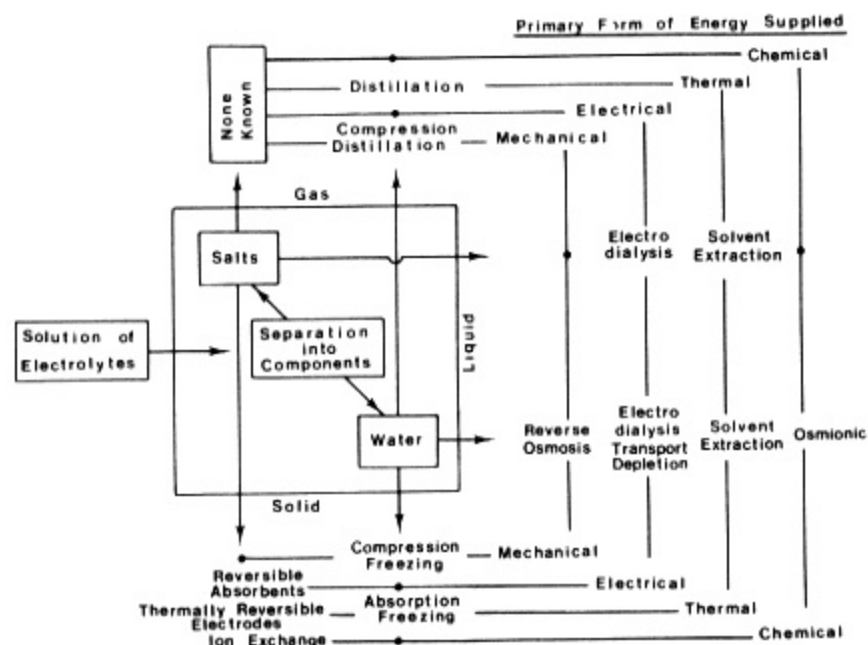


Fig. 1.

Desalination and deionization processes categorized by component separated, phase change, and form of energy supplied.

operated sequentially, and because it produces the highest quality water under ordinary modes of operation, ion exchange is usually the last process in a sequential operation.

Distillation

All of the largest plants existing today for the production of fresh water from seawater use a form of distillation. The product water is both for municipal and industrial uses [12].

Multiple effect evaporators have been used for many years by the chemical process industry, are reliable, have good heat transfer coefficients, and are thermodynamically attractive.

Multistage flash distillation is the process used in almost all large desalting production plants. (See Flash Distillation.) The equipment is simple, the operation is reliable, and manufacturing techniques and engineering design are sufficiently well established to allow dependable, easily operated units to be produced.

Vapor compression evaporators require no source of thermal energy since mechanical compression is sufficient. Energy for the compressors can be supplied by a variety of prime movers although the lack of large size compressors has limited vapor compression to small units. The energy usage of vapor compression is attractive because it is possible to approach the thermodynamic limitations more closely than with other distillation systems.

Although very high quality water can be produced by multiple distillation, the method is very expensive and is used only where extremely pure water is required as in certain laboratory uses. Ordinary distillation processes are capable, if properly designed, of producing water with less than 1 mg/l of dissolved solids.

Reverse Osmosis

Reverse osmosis is a relatively new unit process capable of producing lowconductivity water. More correctly termed "hyperfiltration," deionization is accomplished in this process when a solution of salts is forced by a pressure gradient through a membrane which passes water more readily than it does the ionic constituents. The flux of the water is, to a first approximation, proportional to the effective pressure. The pressure required is, in turn, proportional to the osmotic pressure of the solution being dewatered, and is a function of the concentration of the solution. The rejection of salts by the membrane is a function of the equilibrium distributions of the substrates in the organic polymer-water-salt system and of the water flux itself.

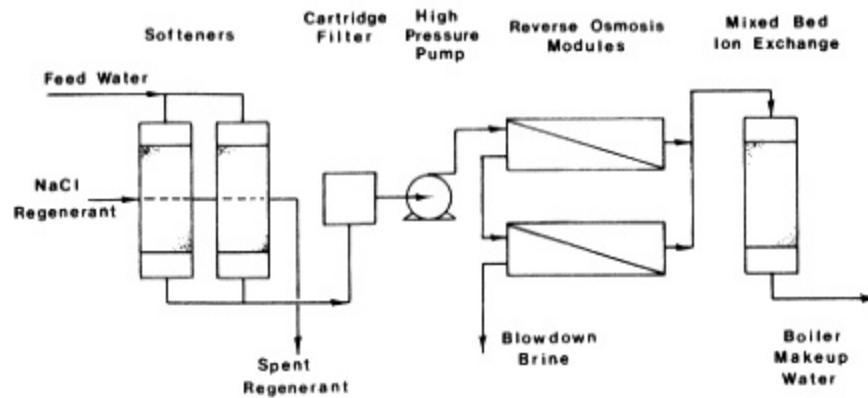


Fig. 2.

Reverse osmosis-ion exchange boiler-makeup treatment system (after Ref. 14).

A combination of reverse osmosis and ion exchange as a sequential deionization process for the production of boiler feedwater is shown in Fig. 2. Pretreatment by softening of the reverse osmosis feed is necessary because the hardness of the feedwater can be sufficiently high to cause precipitation on the reverse osmosis modules as the feed solution is dewatered and concentrated. The product water from the mixed bed effluent stream has a conductance of $0.1 \mu\text{mho/cm}$ and a total solids content of less than 1.7 ppm as CaCO_3 . The reverse osmosis system removes 92% of the salts, the mixed bed demineralizer the remaining 8%. Approximately 89% of the silica is removed by the reverse osmosis system [14].

Ion Exchange

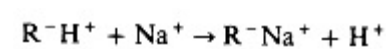
The deionization technology with the longest experience and with the greatest system reliability is ion exchange. In this use it is most often termed "demineralization." When operated to remove ions, the solution is passed through cationic exchange resins in the hydrogen form, and anionic exchange resins in the hydroxyl form so that when the ions are exchanged, hydrogen and hydroxyl ions are released. These combine to form water molecules, and the effluent solutions then have effectively had the removed ions replaced by water molecules.

The ion-exchange resins used in deionization and demineralization are of the conventional types used for other ion-exchange processes [8, 16]. They are typically cross-linked polymers with functional groups attached to the polymer structures and with a sufficiently open structure to permit the transfer of ions into and out of the resin beads. Typical functional groups used in deionization resins are:

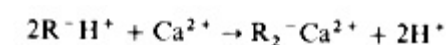
Strong acid,	sulfonic, SO_3^-
Weak acid,	carbonate, CO_3^-
Strong base,	quaternary ammonium, NR_3^+
Weak base,	primary, secondary, tertiary amines, R^+NH

Both the strong acid and strong base resins are capable of exchanging the ions of salts of all degrees of ionization. The functional groups in weak acid and weak base resins are not as highly ionized and are therefore capable of removing strongly, but not weakly, ionized salts. Both types of weakly ionized resins have high capacities for strong acids and bases, respectively, and can be regenerated very efficiently. Both types are used in deionization systems to provide better regeneration economics.

In general, a feedwater is first passed through a strong acid exchanger where the cations are exchanged for the hydrogen ion associated with the resin functionality:

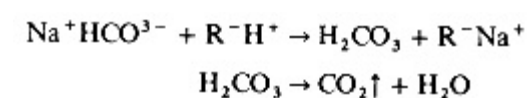


or

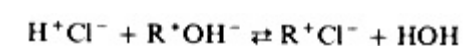


The degree of cation removal depends upon the selectivity of the resin for the particular ion. Selectivity depends upon the ionic valence and upon total solids concentration. The resins in dilute solutions are in general more selective for divalent ions. Thus monovalent ions, Na^+ for example, are likely to appear in the effluent first.

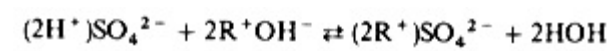
Carbonate, bicarbonate, and silica salts are often found in deionizer feedwaters. When the cation is exchanged for the hydrogen ion, weak acids are formed. The removal of molecular CO_2 by degassing effectively removes the anion and lessens the subsequent required anionic exchange:



The acids formed in the cation exchange are passed through a degassifier to remove CO_2 and then to an anion exchanger or are fed directly to an anion exchanger where the anions are exchanged for hydroxyl ions:



or



or

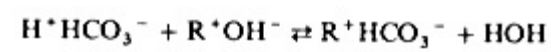


TABLE 2 Typical Ion-Exchange Demineralization Operating Conditions [6]

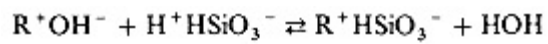
Operating Conditions	Units	Strong Acid H+ Cycle Operation	Strong Base Type I
Service flow	gal/min/ft ³	24	2
Minimum bed depth	in.	30	30
Regenerant level		Depends upon required leakage and capacity	
Regenerant concentration		410% HCl 28% H ₂ SO ₄	4% NaOH (at 120°F for silica)
Regenerant flow rate	gal/min/ft ³	0.52	
Regenerant injection time	lb/ft ³ /h		5
Rinse water requirement	gal/ft ³	40100	50
Rinse rate, displacement	gal/min/ft ³	Equal to regenerant rate	0.25
Rinse rate, final	gal/min/ft ³	Equal to service rate	1

(table continued on next page)

(table continued from previous page)

Operating Conditions	Weak Acid	Weak Base
Service flow rate	14	2
Minimum bed depth	30	3048
Regenerant level	110% of theoretical	Depends upon desired capacity
Regenerant concentration	15% HCl 0.51.0% H ₂ SO ₄	4% NaOH 4% NH ₄ OH
Regenerant flow rate	0.52 HCl 2 gal/min/A3 of 1% H ₂ SO ₄	0.5
Regenerant injection time		
Rinse water requirement	30100	Varies with acid type or temperature
Rinse rate, displacement	0.52	0.5
Rinse rate, final	Equal to service rate	1

or

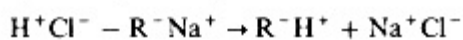
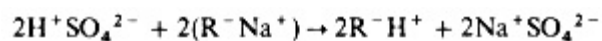


Only the strong base resins are capable of removing both the weak acids (H_2CO_3 , H_2SiO_3) and the strong acids (HCl , H_2SO_4). The weak base resins have about twice the capacity for removing total mineral acidity as that of strong base resins and can be regenerated with soda ash or ammonia.

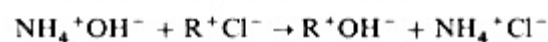
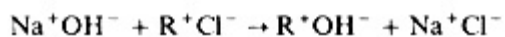
The two ionic types of resin may be mixed together to form a homogeneous bed of mixed resins. Because of the intimate juxtaposition of exchanges, very little ion leakage can occur and a very high quality of water can be produced. Regeneration is complex and is possible only because of the sufficient density difference between the anion and cation resins. Because of the high quality possible and of the regeneration difficulties, mixed beds are often used as secondary polishing units.

Regeneration

Regeneration may be internal or external. Regeneration of the resins is accomplished by passing a solution containing the regenerant ion through the resin to replace the ions removed from solution:



and



Typical service flow rates, regeneration amounts, and rinse rates between deionization and regeneration cycles are shown in Table 2.

Complete regeneration is uneconomic, particularly of the strong acid exchanger, so that some residual ions remain on the resin.

The quality of the effluent from the bed is determined by the relative amounts of Na^+ and H^+ as exchangeable ions on the final resin seen by the solution. Any Na^+ leaking through will continue as a mineral salt through the anion exchangers and will appear in the final effluent.

Waters high in Na^+ cause high cation leakage; waters high in HCO_3^- have low cation leakages. Various solutions to the leakage problem have been used, including bed mixing, counterflow operation, and the use of multiple sequential and mixed exchange beds.

The capacity and leakage expected of a strong acid cation exchanger used in deionization as a function of the amount of regenerant are shown in Fig. 3 with

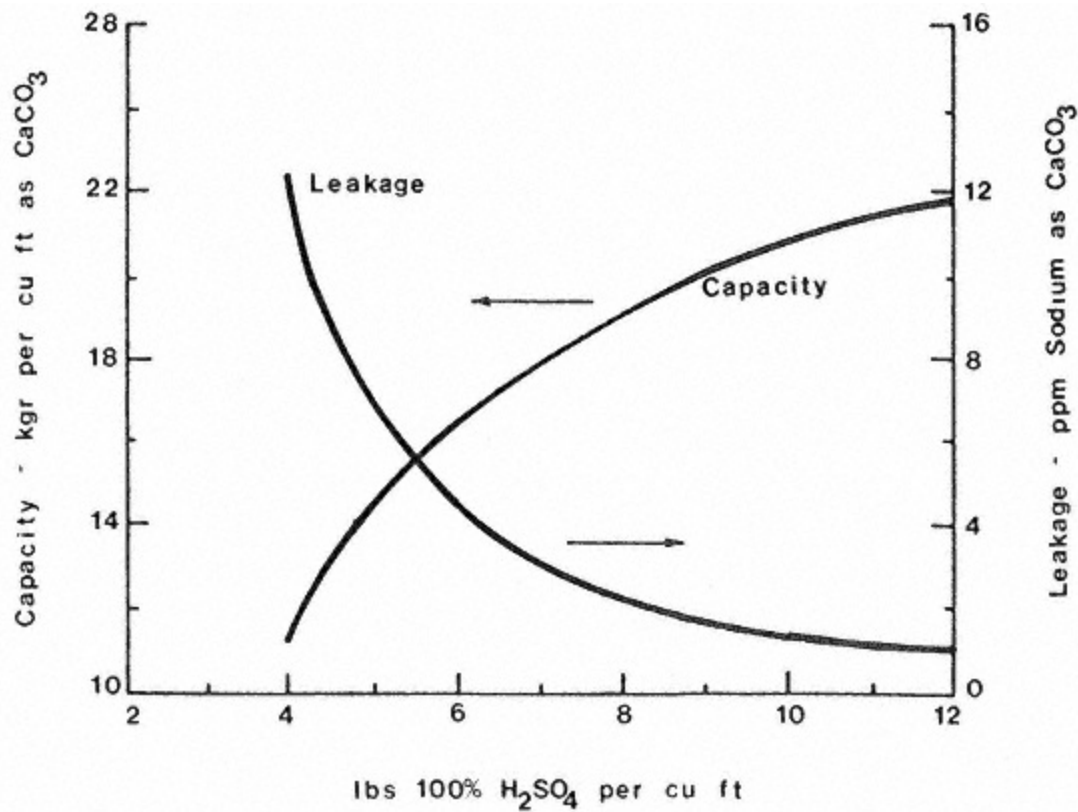


Fig. 3.

Sulfuric acid regeneration of strong acid resin. Influent water with 300 ppm TDS having 50% sodium and 50% alkalinity [6].

sulfuric acid as the regenerant and in Fig. 4 with hydrochloric acid as the regenerant. The capability of sulfuric acid to regenerate the resin is limited by the necessity to minimize formation of calcium sulfate during regeneration. The equivalent weight of sulfuric acid is higher, so at a given weight concentration, fewer regeneration equivalents are available.

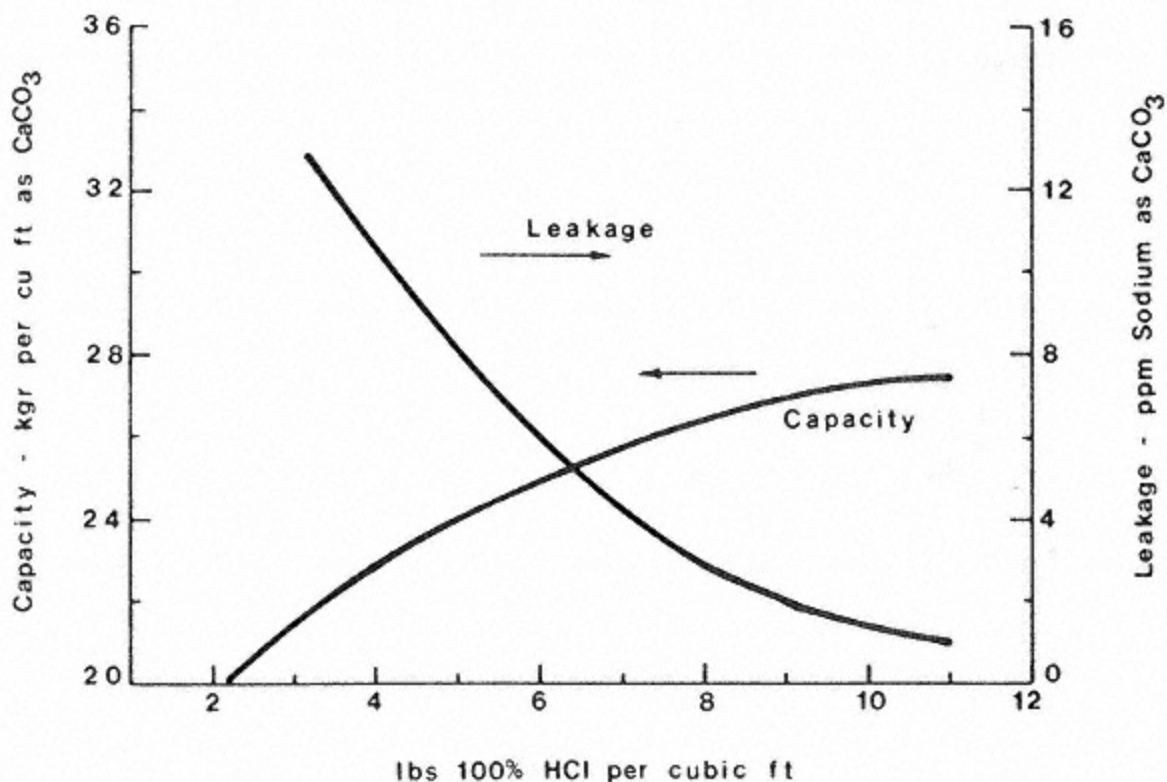


Fig. 4.

Hydrochloric acid regeneration of strong acid resin. Influent water with 300 ppm TDS having 50% sodium and 50% alkalinity [6].

Mixed beds are separable by density differences, the anion resins being lighter so when separated they form an upper layer. In usual mixed bed regeneration systems, a central removal point is used for both the acidic and basic regeneration, with caustic passed down flow and acid up flow to the removal point. A counter blocking flow of water is usually used to prevent bed expansion and to prevent acid from entering the anion bed and caustic from entering the cation bed.

Silica is a problem in many waters and must be removed for hightemperature boiler operation as well as for other uses of high-quality water. Silicic acid is removed by the strong base resin at ambient temperature, but regeneration is most effective with hot caustic 120°F is satisfactory and by allowing longer contact times. The subfills must be capable of withstanding hot caustic in desilicization units.

The selection of the deionizer design is determined by the necessity for removing silica, the effluent quality required, the size of the facility, and the cost of the regenerant. A number of possible configurations is shown in Fig. 5 [1].

The strong acid-weak base two-bed system is used for industrial plants requiring a water quality of 2 to 10 ppm. There is no silica reduction, and this system is not applicable for boiler feed.

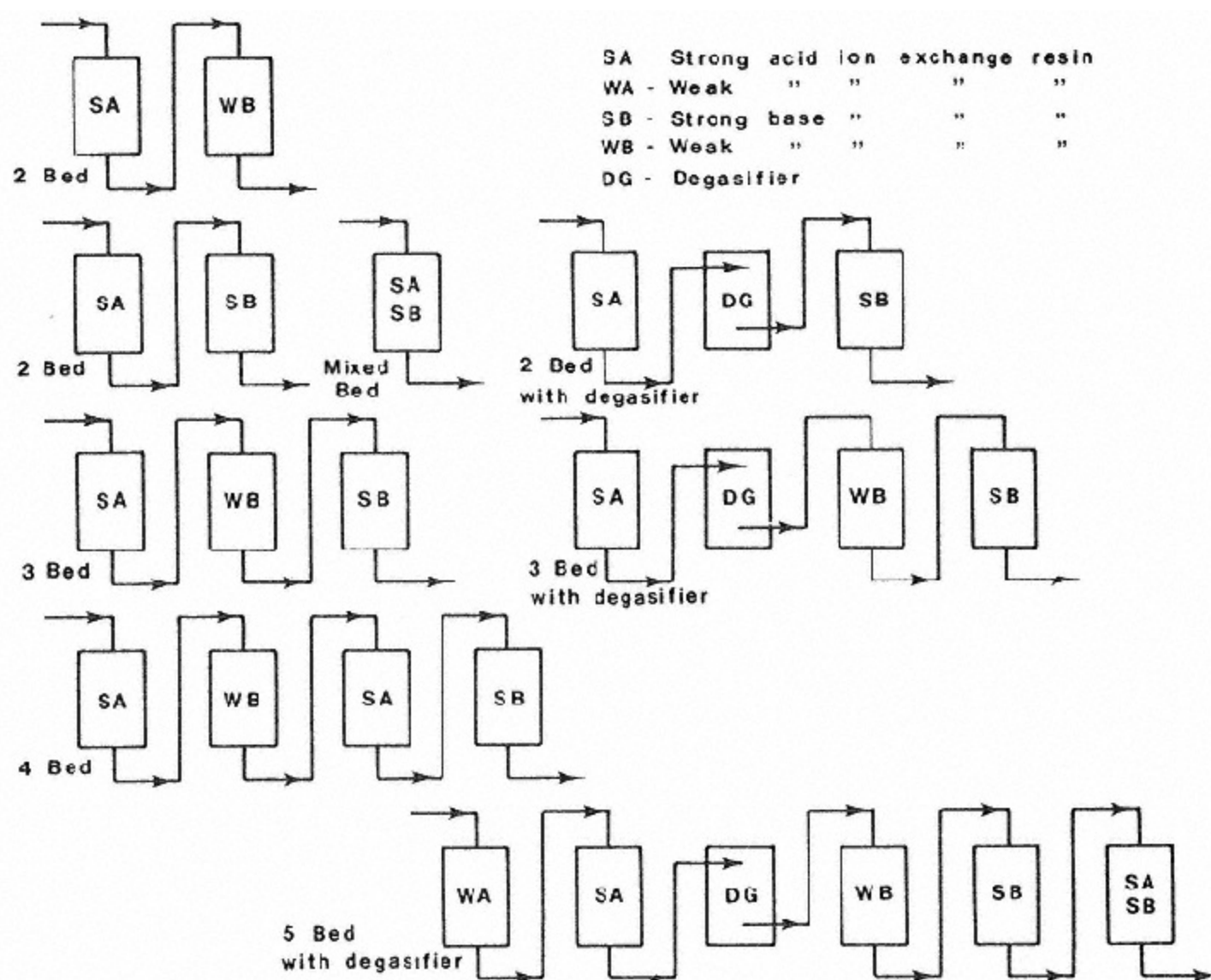


Fig. 5.
 Ion-exchange demineralization system configurations [1, 6].

The strong acid-strong base two-bed system will produce a water of 2 to 3 ppm and will remove silica to a 0.02 to 0.1 ppm level.

The mixed-bed will produce a high water quality and will remove silica, but has a capacity of only 80 to 85% of the same resins in a two-bed system.

The three-bed system with a weak base preceding the strong base will save regenerant with waters high in mineral acidity and often makes decarbonation unnecessary.

The four-bed system saves acid regenerant and is useful in potential high-sodium-leakage water. Regeneration can, and often is, sequential through the cation exchangers.

The use of a decarbonator will reduce the amount of basic regenerant required and reduces the ionic load on the anion unit.

The five-bed system with a degasifier and with a final polish mixed-bed is capable of producing very high quality water with a conductivity in the range of 0.05 to 0.1 $\mu\text{mho/cm}$.

Equipment used in deionization is well developed. Contactors may be fixed-bed columns, the most widely used type, or semicontinuous contactors in which the resin, or columns of resin, are moved to provide a method of carrying out both deionization and regeneration steps more or less simultaneously [11, 16].

Deionized water quality must often be protected in installations requiring constant high quality such as critical and super-critical fossil fuel systems and nuclear fuel reactors. Mixed ion exchangers are used in high-rate (to 100 gal/min/ft²), hot (to 230°F), deep-bed polishers on the condensate systems [7, 18].

Ammonia is often used in such systems for corrosion control. The presence of ammonia in the condensate causes frequent exhaustion of the hydrogen form cation resin, so in these systems the cation resin has been used at a 2-1 volume ratio with the hydroxide form anion resin.

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Electrochemical Engineering: Theory

Francis M. Donahue

Electrochemical engineering is that area of chemical engineering which involves oxidation-reduction chemical reactions at solid or liquid surfaces and the transport processes associated with these heterogeneous reactions. Industries based on electrochemical engineering include chemical synthesis (chlorine, caustic, hydrogen, etc.), metal winning (aluminum, magnesium, zinc, etc.), metal refining (copper, nickel, etc.), metal plating (decorative and protective coatings), and energy conversion and storage (batteries and fuel cells). In addition, corrosion can be studied and effectively mitigated using electrochemical engineering techniques.

Physical Properties of Electrochemical Cells

Most electrochemical processes are effected in devices similar to that shown in Fig. 1. Such a device is called an electrochemical cell. The anode transports the electrons out of the cell into an external circuit while the cathode acts as a sink for electrons from the

external circuit. The principal function of the anolyte and catholyte is to provide electrolytic charge transport within the cell. The separator, if present, serves as a barrier to mixing of anodic and cathodic species. The separator must be capable of transporting charge by ion exchange between the anolyte and catholyte or by restricted electrolyte flow, e.g., by transport through a porous matrix. Ancillary functions of the components of electrochemical cells are given in Table 1.

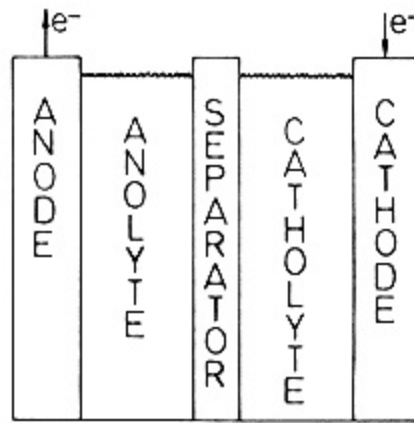


Fig. 1.
Schematic representation of an
electrochemical cell.

TABLE 1 Ancillary Functions of Components of Electrochemical Cells

Component	Function(s)	Example(s)
Anode	a) Actively participates in chemical reaction b) Catalytic surface for reaction	a) Metal refining cells, batteries b) Fuel cells, chlorine production
Anolyte	a) Source of chemical reactant for anode reaction b) Sink for chemical product of anode reaction	a) Chlorine production b) Acid hydrogen fuel cell
Separator	a) Prevent mixing of anode and cathode reactants b) Prevent mixing of anode and cathode products	a) Batteries b) Chloralkali cells
Catholyte	a) Source of chemical reactant for cathode reaction b) Sink for chemical product of cathode reaction	a) Hydrogen production b) Hydroxide production
Cathode	a) Actively participates in chemical reaction b) Catalytic surface for reaction	a) Metal plating, sodium amalgam production b) Hydroxide production

Generalized Electrochemical Reactions

It was noted above that electrochemical engineering involves oxidation-reduction chemical reactions. These so-called redox reactions can be written in the general form



where Red is the reduced form of a chemical species, Ox is the oxidized form of the same species, z is the number of electrons involved in the reaction, and e^- is the symbol for the electron. Examples of some electrochemical reactions and the designation of Red and Ox are given in Table 2. It is evident from Table 2 that the designation is specific to a given reaction and is not limited to the chemical species undergoing the charge transfer process.

Electrochemical reactions which take place at the anode release electrons. The process is one of oxidation. Therefore, one uses the adjectives "anodic" and "oxidation" interchangeably to describe reactions at anodes. In general form an anodic reaction is



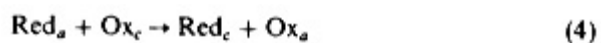
The subscript a is used as an indication that the reaction is taking place at the anode. Although this designation is redundant (i.e., the form of Eq. 2 stipulates that it is an anodic reaction independently of the subscript), it is useful in the discussion of cell reactions (see below).

Electrochemical reactions at cathodes consume electrons. They are reduction reactions. In general form a cathodic or reduction reaction is



The subscript c means that the reaction occurs at the cathode.

In a simple electrochemical cell two electrochemical reactions occur one each at the anode and cathode. In the general form adopted above, the cell chemical reaction is



Equation (4) is the sum of Eqs. (2) and (3). The latter equations are often called half-cell reactions.

TABLE 2 Examples of Reduced (Red) and Oxidized (Ox) Forms of Chemical Species in Electrochemical Reactions

Electrochemical Reaction	Red	Ox
$\text{H}_2 = 2\text{H}^+ + 2e^-$	H_2	H^+
$2\text{H}_2\text{O} = 4\text{H}^+ + \text{O}_2 + 4e^-$	H_2O	$\text{H}^+ \text{ O}_2$
$\text{Ag} + \text{Cl}^- = \text{AgCl} + e^-$	Ag Cl^-	AgCl
$\text{Fe} = \text{Fe}^{2+} + 2e^-$	Fe	Fe^{2+}
$\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$	Fe^{2+}	Fe^{3+}

Thermodynamic Properties of Electrochemical Cells

Thermodynamic properties of electrochemical cells are obtained using the methods of classical thermodynamics. The most important thermodynamic property of electrochemical cells is the free enthalpy, ΔG . (The symbol ΔG has also been called free energy, Gibbs free energy, and Gibbs function in the literature of thermodynamics.) As in the case of classical thermodynamics, when the free enthalpy is zero, the cell is at equilibrium. Likewise, a negative value of the free enthalpy means that the cell can operate spontaneously. Such electrochemical cells are capable of producing energy; batteries and fuel cells possess this property. When the free enthalpy is positive, the cell cannot operate spontaneously. In order to effect the cell chemical reaction for cells with this property, it is necessary to apply electrical energy to the cell; all electrometallurgical, electroplating, and electrosynthesis processes in current practice belong to this class of electrochemical cells.

The cell voltage, E , for an electrochemical cell is related to the free enthalpy of the reaction per mole of basis species by

$$E = -\Delta G/nF \quad (5)$$

where n is the number of equivalents per mole of basis species (it is numerically equal to $z/|v|$) and F is the Faraday constant (2.306×10^4 cal/V-equiv). Energy-producing electrochemical cells have positive cell voltages while energy-consuming cells have negative cell voltages.

The cell voltage for an electrochemical cell derives from electrical potential differences in various parts of the cell. Consider the simplest type of electrochemical cell (see above) shown schematically in Fig. 2. Assume further that no current passes through the cell and that no "parasitic" electrochemical reactions take place at either electrode-solution interface. The measured cell voltage, E , for this configuration (which is equal to that calculated from Eq. 5) is given by

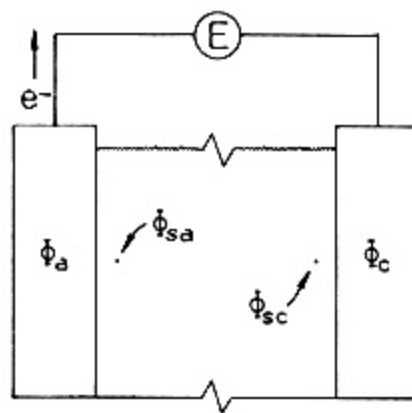


Fig. 2.
Schematic representation of the simplest
electrochemical cell.

$$E = (\Phi_a - \Phi_{sa}) + (\Phi_{sa} - \Phi_{sc}) + (\Phi_{sc} - \Phi_c) \quad (6)$$

where Φ_a is the electric potential of the bulk phase of the anode, Φ_{sa} is the electric potential of the solution a short distance (5100 Å) from the cathode-solution interface, Φ_{sc} is the electric potential of the solution a short distance (5100 Å) from the cathode-solution interface, and Φ_c is the electric potential of the bulk phase of the cathode. The potential differences at the respective electrode-solution interfaces derive from the chemical potentials of the species in the redox reactions and the distribution of charged (ionic) species at the respective electrode-solution interfaces.

Since no current flows through the cell and a single electrolytic solution is present, $\Phi_{sa} = \Phi_{sc}$, i.e., there is no potential difference across the electrolytic solution. Then Eq. (6) becomes

$$E = \Phi_a - \Phi_c \quad (7)$$

Figure 3 shows two examples of electrochemical cells in terms of the various electric potentials. Figure 3(a) is an example of a potentially energy-consuming cell while Fig. 3(b) is an example of a potentially energy-generating cell.

Although most of the cells discussed in this section are not in the formal sense at equilibrium (i.e., $\Delta G \neq 0$), they are commonly called equilibrium cells

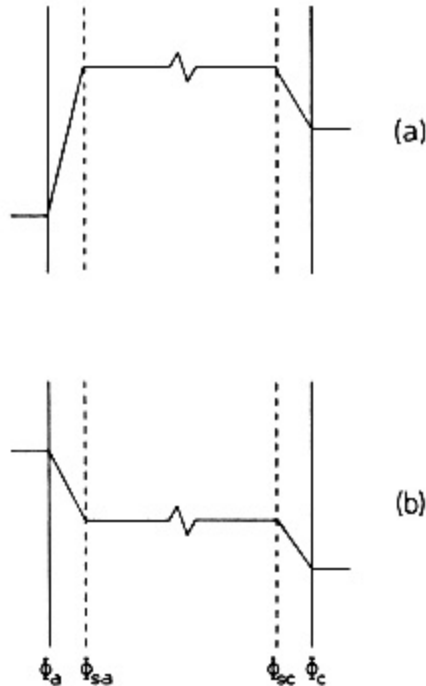


Fig. 3.
Electric potential distribution in cells like
those in Fig. 2 showing potentially
energy-consuming
(a) and energy-producing
(b) types.

because the cell voltage can be computed using the methods of equilibrium thermodynamics once the cell chemical reaction is established.

The cell voltages for the following types of cells cannot be computed in the manner mentioned above:

- a. Cells with a separator and two different electrolytic solutions
- b. Cells through which a current is flowing
- c. Cells in which "parasitic" reactions occur in the absence of a current

The cell voltage for cells described by a is (see Fig. 4)

$$E' = (\Phi_a - \Phi_{sa}) + (\Phi_{sa} - \Phi_{sa}) + (\Phi_{sa} - \Phi_{sc}) + (\Phi_{sc} - \Phi_{sc}) + (\Phi_{sc} - \Phi_c) \quad (8)$$

where Φ_{sa} and Φ_{sc} are the electrical potentials of the separator at the anolyte-separator and catholyte-separator interfaces, respectively. Inserting Eq. (6) in Eq. (8) and simplifying, one finds

$$E' = E + (\Phi_{sa} - \Phi_{sc}) \quad (9)$$

Therefore, the cell voltage computed from thermodynamic considerations, E , is attenuated by a so-called liquid junction potential. Methods of computing liquid junction potentials are available [47]. Cells described by b and c will be treated subsequently.

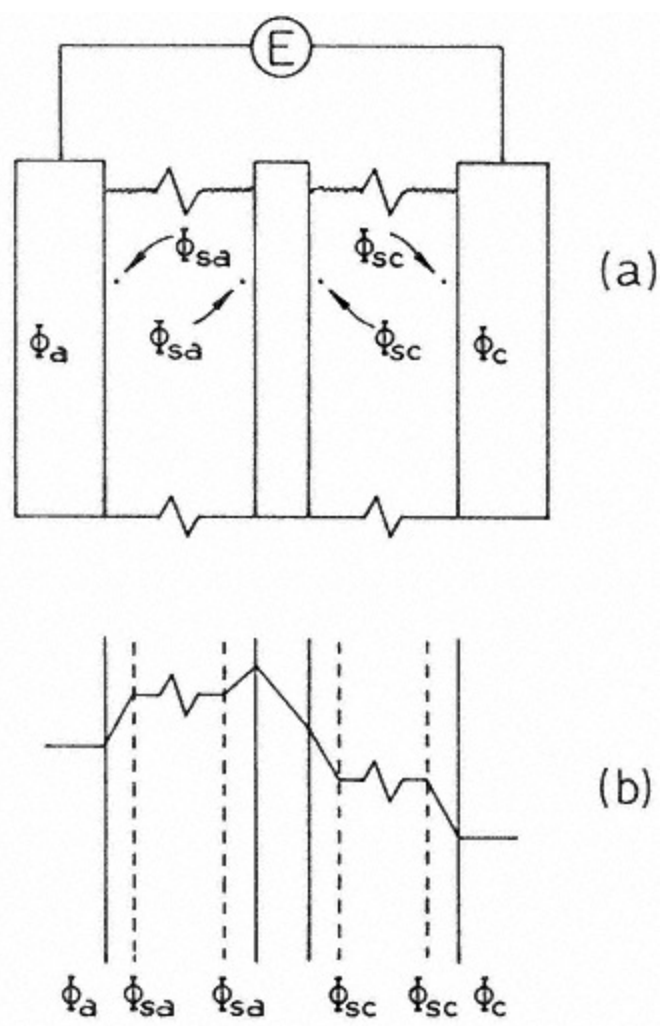


Fig. 4.
Schematic representation
(a) and electric potential distribution
(b) for a cell with a separator and two different electrolytic solutions.

Thermodynamic and Kinetic Properties of Single Electrodes

Experimental studies of electrochemical reactions normally focus on electrode processes at single electrodes. The potential at a single electrode is measured in a circuit similar in concept to that shown in Fig. 2. The electrode to be studied is assumed to be the cathode in the cell and is called the test electrode. The assumed anode in the circuit is called a reference electrode. The electrode potential, ϕ_m , for a redox reaction is defined as

$$\phi_m = \Phi_{sm} - \Phi_m \tag{10}$$

where the subscript m represents either anode or cathode. The measured cell voltage for the circuit is (from Eqs. 6 and 10)

$$E = \phi_t - \phi_r \tag{11}$$

where ϕ_t is the electrode potential of the test electrode and ϕ_r is the electrode potential of the reference electrode.

The normal standard for reference electrodes is the redox reaction



At unit fugacity of hydrogen gas and unit activity of hydrogen ion, the electrode potential for this redox reaction is defined as 0.000 V and is called the "standard hydrogen electrode" (SHE). Table 3 gives some values of the reversible electrode potentials (see definition below) of other reference electrodes. More details concerning reference electrodes can be found in Ives and Janz [9]. When electrode potentials for redox reactions are reported in the literature, the author always identifies the reference electrode used in the measurements.

When an electrochemical reaction at an isolated electrode (i.e., one which is not connected to a power supply or another electrode unless by means of a high impedance voltage-measuring device) is in true chemical equilibrium, it exhibits a unique electrode potential called the reversible electrode potential, ϕ_0 . For the redox reaction given in Eq. (1), the reversible electrode potential is calculated from

TABLE 3 Reversible Electrode Potentials of Selected Reference Electrodes at 25°C [8]

Electrode Reaction	Electrolyte	ϕ_0 (V vs SHE)
2Hg + 2Cl ⁻ = Hg ₂ Cl ₂ + 2e ⁻ (calomel electrode)	satd KCl	0.241
	1.0 m KCl	0.281
	1.0 M KCl	0.280
	0.1 M KCl	0.334
Hg + 2OH ⁻ = HgO + H ₂ O + 2e ⁻	satd Ba(OH) ₂	0.146
	satd Ca(OH) ₂	0.192

$$\phi_0 = \phi^\circ + \frac{RT}{zF} \ln \left(\frac{Ox^{|\nu_{Ox}|}}{Red^{|\nu_{Red}|}} \right) \quad (13)$$

where ϕ° is the standard single electrode potential for the redox reaction. Table 4 contains values of ϕ° (with respect to the "standard hydrogen electrode") for many reactions of interest in electrochemical engineering.

When a redox reaction at an electrode (isolated or otherwise) is not at equilibrium, it is said to be "polarized," i.e., it is in a perturbed state. The source of this perturbation from the equilibrium state is normally due to the flow of charge across the electrode-solution interface. The measure of this perturbation in terms of electrode potential is called total overpotential, η_{tl} , and is defined as

$$\eta_{tl} = \phi_i - \phi_0 \quad (14)$$

where ϕ_i is the perturbed electrode potential. When the overpotential is positive, the redox reaction is said to be "polarized anodically," i.e., the net reaction is anodic. Similarly, the electrode is "polarized cathodically" when the overpotential is negative.

More than one type of overpotential is possible in electrochemical systems. When the rate of the redox reaction is small compared to the rate of mass

TABLE 4 Selected Standard Single Electrode Potentials in Water at 25°C

Electrode Reaction	ϕ° (V vs SHE)
$PbSO_4 + 2H_2O = PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$	+1.685
$Cl^- + 3H_2O = ClO_3^- + 6H^+ + 6e^-$	+1.45
$2Cl^- = Cl_2 + 2e^-$	+1.360
$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$	+1.23
$2H_2O = O_2 + 4H^+ + 4e^-$	+1.229
$H_2O_2 = O_2 + 2H^+ + 2e^-$	+0.682
$Fe(CN)_6^{4-} = Fe(CN)_6^{3-} + e^-$	+0.49
$2Ag + 2OH^- = Ag_2O + H_2O + 2e^-$	+0.345
$Cu = Cu^{2+} + 2e^-$	+0.337
$Cu^- = Cu^{2+} + e^-$	+0.153
$H_2 = 2H^+ + 2e^-$	0.000
$N_2H_5^+ = N_2 + 5H^+ + 4e^-$	-0.23
$Ni = Ni^{2+} + 2e^-$	-0.250
$Pb + SO_4^{2-} = PbSO_4 + 2e^-$	-0.359
$Fe = Fe^{2+} + 2e^-$	-0.440
$Zn + 3OH^- = HZnO_2^- + H_2O + 2e^-$	-0.72
$Zn = Zn^{2+} + 2e^-$	-0.763
$Cd + 2OH^- = Cd(OH)_2 + 2e^-$	-0.809
$Fe + 2OH^- = Fe(OH)_2 + 2e^-$	-0.877
$Zn + 2OH^- = Zn(OH)_2 + 2e^-$	-1.245
$Mg = Mg^{2+} + 2e^-$	-2.363
$Mg + 2OH^- = Mg(OH)_2 + 2e^-$	-2.69

transport of reactants to or products from the interface, activation overpotential, η , operates. Activation overpotential arises essentially from changes in the chemical potential of reactants and products during the reaction. When the rate of the redox reaction is approximately the same order of magnitude as the rate of mass transport, concentration overpotential, η_{conc} , operates. This overpotential derives from differences in concentration of the species in the redox reaction between the bulk of the solution and the interface. Figure 5 is a schematic representation of a redox process under the influence of concentration overpotential. As shown in Fig. 5, electrodes where concentration overpotential is present normally operate under activation overpotential also. Under these conditions, Eq. (14) becomes

$$\eta_{\text{st}} = \eta + \eta_{\text{conc}} \quad (15)$$

As noted above, the flow of charge across the interface leads to perturbation of the redox reaction from the equilibrium state. The manifestation of the flow of charge across the interface for most electrochemical systems is an electric current, I , in an external circuit. This current is often an extensive property of the redox reaction. In order to minimize the extensive nature of this property, it is useful to divide the electric current in the external circuit by the surface area of the electrode in contact with the electrolytic solution. This quotient is called the current density, i .

The general equation relating current density and activation overpotential was first formulated by Butler [10]. A convenient form of the equation is

$$i = i_0 (\exp [\eta/\beta_a] - \exp [-\eta/\beta_c]) \quad (16)$$

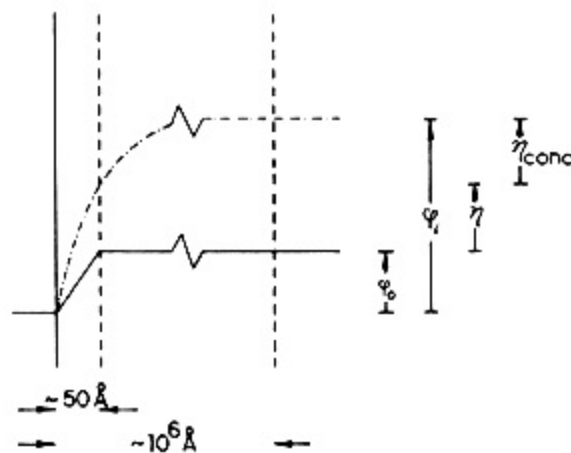


Fig. 5.
Electric potential distributions of a single electrode at equilibrium (solid lines) and under the combined effects of activation and concentration overpotentials (dash-dot curve)

where i_0 is the exchange current density and β_a and β_c are empirical constants which are properties of the redox reaction and the electrode material. The exchange current density is a manifestation of the dynamic nature of the equilibrium state and a measure of the intrinsic reactivity of the redox reaction; the larger i_0 , the greater the reactivity. Inspection of Eq. (16) reveals the sign convention for current density in normal usage, i.e., anodic current is positive while cathodic is negative.

The exchange current density can normally be described by the empirical equation

$$i_0 = k^\circ [\text{Red}]^\rho [\text{Ox}]^\omega \quad (17)$$

where k° is a specific rate constant at the standard electrode potential, $[\text{Red}]$ and $[\text{Ox}]$ are the concentrations of the respective species, and ρ and ω are reaction orders. The value of the specific rate constant is dependent upon the redox process, the electrode material, and the temperature.

The electrode potential-current density behavior of a typical redox reaction under activation overpotential conditions is shown in Fig. 6. The upper curve is that for anodic polarization while the lower curve is cathodic polarization. The absolute values of the slopes of the linear portions of the curves are the so-called Tafel slopes, i.e., β . One may determine the exchange current density by extrapolating the linear portions of the curves to the equilibrium electrode potential. Series of experiments of this type are used to evaluate the unknown parameters in Eq. (17).

The equation relating concentration overpotential and current density for a redox reaction (e.g., Eq. 1) is

$$\eta_{\text{conc}} = \mp RT/zF \ln(1 - i/i_0) \quad (18)$$

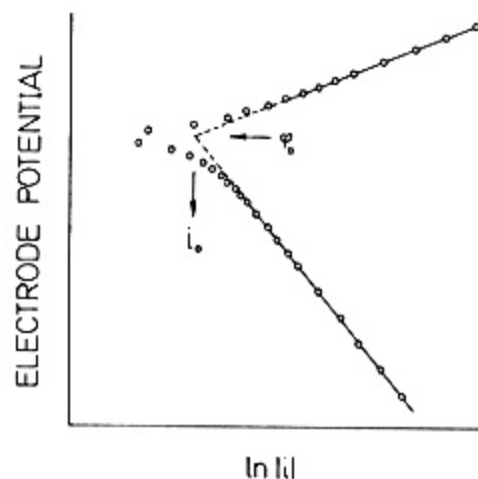


Fig. 6.
Electrode potential-current density behavior
of a redox reaction under activation control.

where i_l is the limiting current density. The negative sign is used for anodic processes; the positive sign, for cathodic processes. The limiting current densities for redox processes where reactant consumption is mass transfer limited for anodic and cathodic processes, respectively, are

$$i_l = z F k_{ca} [\text{Red}] \quad (19)$$

$$i_l = -z F k_{cc} [\text{Ox}] \quad (20)$$

where F is the Faraday constant ($9.65 \times 10^4 \text{ A} \cdot \text{s/equiv}$),* the concentrations are those in the bulk of the solution, and k_{ca} and k_{cc} are the mass transfer coefficients for the anodic and cathodic processes, respectively, and can be computed from standard mass transfer correlations for the appropriate geometry and flow regime [11, 12]. When transport of the product of the reaction is mass transfer limited, the anodic and cathodic limiting current densities, respectively, are

$$i_l = z F k_{ca} ([\text{Ox}]_{\text{satd}} - [\text{Ox}]) \quad (21)$$

$$i_l = -z F k_{cc} ([\text{Red}]_{\text{satd}} - [\text{Red}]) \quad (22)$$

where the subscript "satd" means that the concentration of the species so designated is saturated at the electrode-solution interface. Equation (18) shows that, for $i \ll i_l$, $\eta_{\text{conc}} = 0$, i.e., no concentration difference exists between the bulk and the interface. For $i \rightarrow i_l$, $|\eta_{\text{conc}}|$ tends toward infinity. Figure 7 shows the electrode potential-current density behavior of a cathodic process with the transition from activation control to mass transport control.

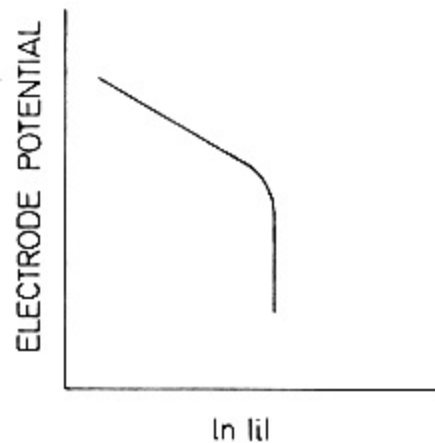


Fig. 7.
Electrode potential-current density
behavior of a cathodic reaction showing
the transition from activation control to
mass transport control with increasing
cathodic overpotential.

* In thermodynamic calculations the Faraday constant has the value given before (see Eq. 5); in kinetic or transport calculations it has the value given here.

Until this point in the discussion it has been assumed that only one redox reaction operates at a single electrode. In practice, one often encounters isolated electrodes where two or more redox reactions take place. Electrodes with these properties have been called mixed electrodes [13]. Most corrosion processes, many self-discharge reactions in batteries, and electroless plating reactions are examples of isolated mixed electrodes. Electrodes in most electrolysis and electroplating cells where the current efficiency (ratio of the current producing the desired product to the total current flowing at an electrode) is less than unity are also examples of mixed electrodes. Figure 8 is a schematic representation of the simplest isolated mixed electrode, i.e., a single electrode where one anodic and one cathodic partial process operate. The operation of an isolated mixed electrode is analogous to a short-circuited battery, i.e., an anodic partial process and a cathodic partial process operate at a single electrode potential (called the mixed potential) and at a rate which conserves charge. If sufficient kinetic and thermodynamic data are available for the partial processes, the mixed potential and the mixed current density (proportional to the rate of the respective partial processes) can be computed [14]. Mixed potential systems are those electrodes which have been associated with "parasitic" reactions in the discussions above.

Properties of Electrochemical Cells under Current Loads

Consider an electrochemical cell like that shown schematically in Fig. 2 (technical examples of cells like this are electrorefining, electroplating, some electrosynthesis, and some fuel cells) under a current load. Figure 9 shows the electric potential distribution in the cell at open circuit (solid lines) and under a current load (dash-dot lines). (For convenience of representation, the electric potential of the anode has been held constant. This is not a necessary property of electrochemical cells.) The cell voltages for these two circumstances can be represented by inserting the appropriate form of Eq. (10) in Eq. (6), i.e.,

$$E_o = \phi_{oc} - \phi_{oa} \quad (23)$$

and

$$E_I = \phi_{ic} - \phi_{ia} + (\Phi_{aa} - \Phi_{ac}) \quad (24)$$

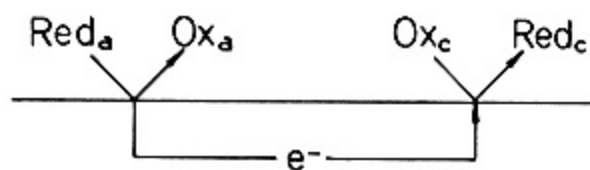


Fig. 8.
Schematic representation of the simplest isolated mixed electrode.

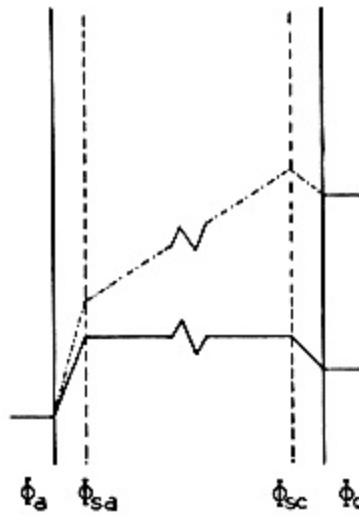


Fig. 9.

Electric potential distribution in an energy-consuming cell at open circuit (solid lines) and under a current load (dash-dot lines).

where E_o is the open-circuit cell voltage; ϕ_{oc} and ϕ_{oa} are the equilibrium electrode potentials of the cathode and anode, respectively; E_I is the cell voltage under a current load, I ; ϕ_{ic} and ϕ_{ia} are the perturbed electrode potentials of the cathode and anode, respectively; and $(\Phi_{sa}\Phi_{sc})$ is a voltage drop in the electrolyte due to the flow of the current. The latter is often represented by

$$(\Phi_{sa} - \Phi_{sc}) = -IR_e \quad (25)$$

where R_e is the resistance of the electrolytic solution. For an electrochemical cell with parallel-plate electrodes, the resistance is

$$R_e = \rho l/A \quad (26)$$

where ρ is the specific resistivity of the electrolytic solution, l is the spacing between the electrodes, and A is the electrode area in contact with the electrolyte. For cells with concentric cylindrical geometry,

$$R_e = \frac{\rho \ln(r_o/r_i)}{2\pi L} \quad (27)$$

where r_o is the radius of the outside electrode, r_i is the radius of the inside electrode, and L is the electrode height in contact with the electrolyte.

Substituting Eq. (25) in Eq. (24), subtracting Eq. (23), rearranging the result, and substituting Eq. (14), one obtains

$$E_I = E_o + \eta_{tl,c} - \eta_{tl,a} - IR_e \quad (28)$$

where $\eta_{t,c}$ and $\eta_{t,a}$ are the total overpotentials at the cathode and anode, respectively. Since the total cathodic overpotential becomes increasingly negative with increasing current density while the total anodic overpotential increases with increasing current density, Eq. (28) shows that the cell voltage decreases with increasing current. This is characteristic of both energy-producing and energy-consuming cells. [In the fields of electrosynthesis and electroplating the absolute value of the cell voltage is normally reported (but usually not identified as such). Therefore, in these fields it is claimed that the cell voltage increases with increasing current.]

The cell voltage of electrochemical cells similar to that shown schematically in Fig. 1 (technical examples of cells like this are many electrosynthesis cells and most batteries) is

$$E_t = E_o - \phi_{LJ} + \eta_{t,c} - \eta_{t,a} - IR_{int} \quad (29)$$

where ϕ_{LJ} is the liquid junction potential and R_{int} is the internal resistance of the cell. The liquid junction potential is defined as (see Eq. 9)

$$\phi_{LJ} = \Phi_{sc} - \Phi_{sa} \quad (30)$$

and the internal resistance is

$$R_{int} = R_{ea} + R_s + R_{ec} \quad (31)$$

where R_s is the resistance of the separator and R_{ea} and R_{ec} are the resistances of the anolyte and catholyte, respectively (see above).

Considerations in Electrochemical Cell Design

Equation (28) provides insight into the factors which are desirable features in the design of electrochemical cells. Consider an electrochemical cell which is to be designed for a specified rate of production of a fixed cell current. (This discussion applies equally well to the design of energy-producing cells.) In order to minimize the energy required for this cell, one needs to achieve the largest positive cell voltage (recall that the cell voltage for energy-consuming cells is inherently negative). Therefore, one needs to minimize the electrolyte resistance and the absolute values of the respective overpotentials. Both may be achieved by increasing the areas of the electrodes. Since electrodes are usually expensive, an optimization based on considerations of investment and operating costs is usually indicated.

In addition, the absolute values of the overpotentials can be decreased for cases of activation overpotential control by increasing the respective exchange current densities. This can be effected by raising the temperature, increasing the concentration of reactant, and, at times, changing the electrode materials. Design based upon this approach requires an intimate knowledge of the

kinetics of the respective electrode processes (see above). Without specific knowledge of the dependence of the exchange current density on concentration, temperature, etc., it is not possible to indicate a priori on what basis an optimization might be effected. While increasing the temperature will also decrease the electrolyte resistance, increasing the reactant concentration does not necessarily decrease the electrolyte resistance [15].

In systems where concentration overpotential plays a major role, the cell voltage can be increased by increasing the rate of mass transport to the offending electrode(s), e.g., by increasing the velocity of the electrolyte flow. In cases like these, an optimization based on pumping requirements and cell voltage is indicated [16].

From the foregoing it is evident that sufficient knowledge exists concerning the behavior of cells to make simulation and optimization of electrochemical systems more-or-less routine. However, published reports of cell simulation [17, 18] and optimization [16] are not as prevalent as one would expect. It is probable that most specific cell simulations and optimizations which do exist are available only for in-house use in industry.

Nonuniformities in Electrochemical Cells

In the treatment given above, no consideration was given to nonuniform distributions of electrode potential and current density in electrochemical cells. Solutions of nonuniformities are normally specific for the particular cells, electrolytes, polarization, etc. Therefore, a few instances will be reviewed below for illustrative purposes.

Gas evolution at one or both of the electrodes in a cell causes a nonuniform effective electrolyte resistance due to entrapment of gas bubbles in the electrolyte stream(s) [19]. The nonuniform electrolyte resistance causes a nonuniform current density at the electrodes.

Irregularly shaped electrodes (characteristic of electroplating and many electrosynthesis systems) lead to nonuniform current density distributions [2022]. Systems of this sort are analogous to nonuniform, steady-state temperature distributions in heat conduction problems frequently encountered in chemical engineering practice. The electric potential of the electrolyte is analogous to temperature while the current density at the electrodes is analogous to the heat flux.

There are a number of electrochemical systems which are analogs of heterogeneous catalysis. Flooded porous electrodes [2327] (the extended surface area electrodes in batteries) and barrel electroplating [28] are examples of electrochemical systems where the interactions among electrode kinetics and transport processes lead to nonuniform current density distributions within the electrode matrix. The mathematical solutions for the reaction distributions are similar to those for effectiveness factor calculations in heterogeneous catalysis.

Most fuel cell electrodes involve localized reactions at gas-liquid-solid regions. The

transport processes and the electrode kinetics of these systems have been examined in detail [29, 30].

Applications in Other Phases of Chemical Engineering

Electrochemical systems have been used extensively in the study of liquid phase mass transport phenomena and in the establishment of mass transfer correlations [3135]. The main advantage of electrochemical methods over other methods is the property that the flux of the reactant species to the surface (or product, away) is proportional to the current flowing in the external circuit. Therefore, the flux is a measured parameter rather than one calculated from other measured properties [31]. The only limitation to the use of this method is that only electrochemically active species can be studied; however, with the large number of redox reactions available, this is not a severe limitation for the establishment of mass transfer correlations.

Since the instantaneous flux of a species at an electrode is the measured property, fluctuations of mass transport processes can be measured directly and easily using electrochemical techniques [33]. Such measurements have been used in detailed studies of turbulence phenomena [36].

Some other applications, e.g., corrosion control, are treated elsewhere in this Encyclopedia while potential applications have been the topic of research symposia [37, 38].

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Electrochemical Process Design and Operation

Ronald L. Dotson

Introduction

Invention of the electric dynamo at the turn of the century spawned new fields of study and development using the electron as a reagent for chemical production [19].

Electric energy is by far the cleanest and most useful energy form found on this planet. Man has not, however, been able to fully utilize it for his varied needs because of the technical limitations on his ability to generate, store, and consume it [15, 914].

During the course of the past 50 years, numerous applications of electric power have been used to produce oxidation and reduction reactions in electrolytic cells. These industrial developments were largely empirical during this period, so theory lagged miserably behind electrochemical engineering applications [69].

The development of practical electrochemical systems exposes the engineer to many rigorous scientific problems, and the difficulty of evaluation and scale-up of such systems increases with the complexity of the mass transport and charge transfer involved [1068].

This discussion of the operation of electrochemical processes describes some typical industrial units that are now used.

Commercial Electrochemical Reactors

The primary examples of industrial electrochemistry are in the production of chlorine, chlorate, perchlorate, caustic soda, aluminum, hydrogen, and oxygen from water electrolysis.

Chloralkali Cells

Chloralkali technology involves three general cell types (Fig. 1): the flowing-mercury cathode, the diaphragm, and the membrane. Each system offers its own technoeconomic advantages, and the first two have undergone many developments during the past 75 years. During the past 10 years there has been a resurgence of interest in cell designs because of increased costs and the availability of new materials, and thus considerable changes have been made in their sizes and capacities and the membrane cell, an entirely new type, was invented [1517, 67, 68, 8091].

Mercury Cells

In the amalgam cell process for chlorine production, an aqueous solution of a chloride salt is efficiently electrolyzed (Fig. 2). Halogen gas evolves at a graphite or metal anode, while the alkali metal of the salt deposits with zero electrovalence on and into a mercury cathode. This free alkali metal, i.e., lithium, sodium, or potassium, deposits on and diffuses into the mercury to form an amalgam which can flow and can be withdrawn from the electrolysis compartment. The amalgam, once formed, is very stable and can be set aside in

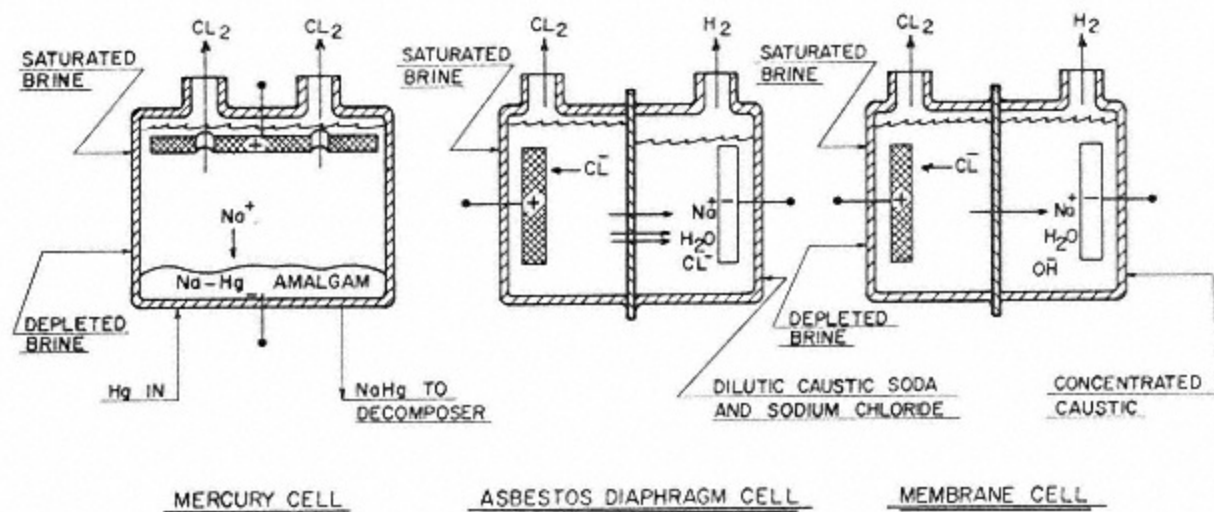


Fig. 1.

Comparison of the basic electrolytic cells used to produce chlorine and caustic in the commercial market.

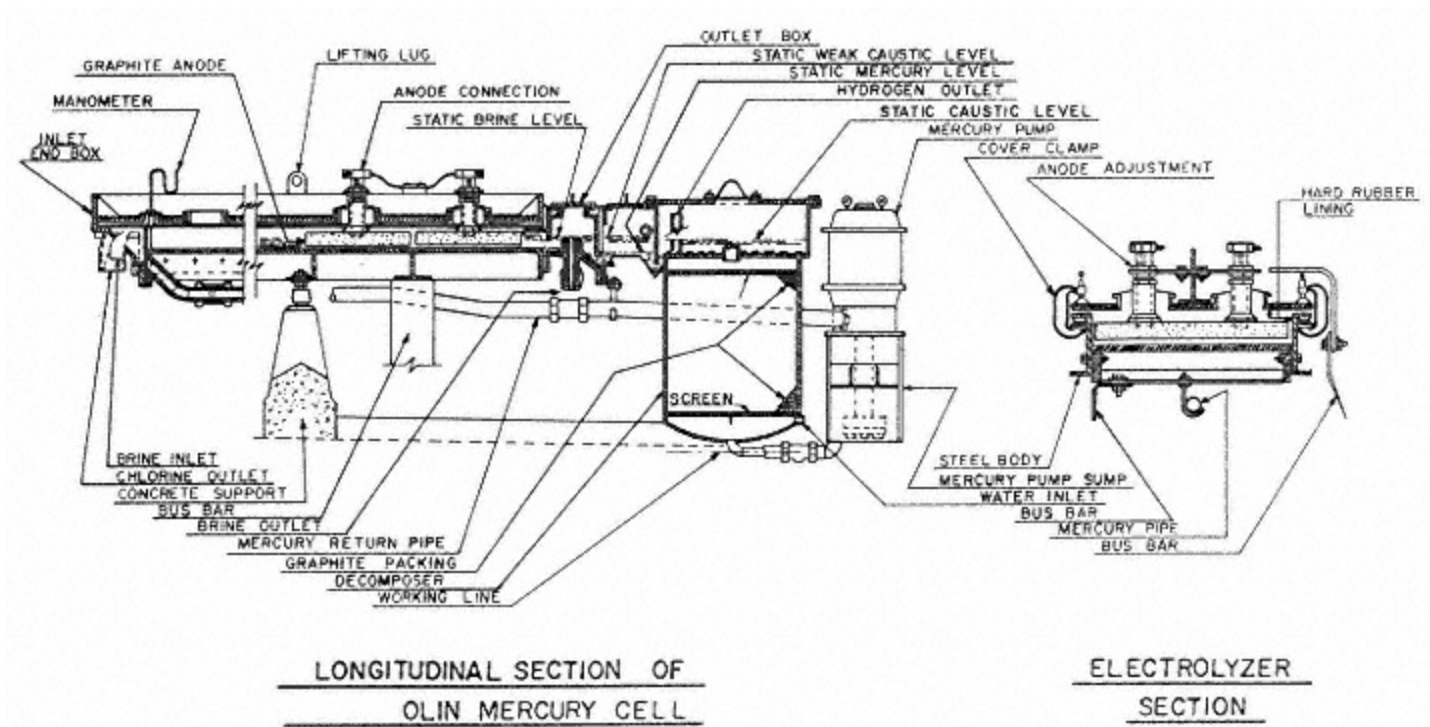


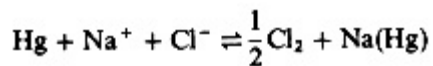
Fig. 2.

Sectional view of a typical chlorine-caustic mercury cell in longitudinal section from electrolyzer to denuder.

storage or used in a number of different processes, such as in production of alkali metals, metal alcoholates, sulfites, hydrosulfites, chlorite, and nitrite [1518].

By far the greatest use for the amalgam cell is in producing caustic soda and chlorine from common salt. In this case the sodium amalgam has a strength of 0.1 to 0.3 wt.% Na° in Hg, and reacts according to [6971]:

Electrolyzer:



Decomposer:



In most plants the sodium amalgam is decomposed with water to form caustic soda and hydrogen gas; the hydrogen is subsequently burned in air for boiler heat or used in synthesis. The caustic produced in this manner is exceptionally pure because of the highly purified water feed and can be made in strengths up to 73 wt.% caustic. After the water in the denuder strips the sodium from the amalgam, the mercury is returned to the electrolysis cell by a pump. For the manufacture of caustic alkali it is customary to attach a decomposition chamber, or decomposer, to each cell (Fig. 2), keeping the mercury in each unit independent and isolated from the other electrolyzer units in the cell room.

The decomposer attached to the electrolyzer can be designed as a vertical tower packed with lumps of broken graphite. The packing is held between screens compressed with large jack screws. A distribution plate spreads the amalgam uniformly and evenly over the top of the packing. The amalgam enters the top through a double-seal to ensure that the minimum amount of chloride enters into the decomposer from the electrolyzer. Purified water enters at the bottom of the decomposer below the packing, and then overflows as a 50 or 73% solution of sodium hydroxide from an outlet located above the top of the packing.

Sodium amalgam decomposes upon contact with the graphite packing, water, sodium hydroxide, and hydrogen. Hydrogen is piped from a connection on the top of the decomposer. Mercury collects in a sump at the bottom of the decomposer and flows to a sump-type centrifugal pump. This pump delivers the stripped mercury to the inlet end of the electrolyzer in a steel pipe at such a rate that about 0.2 wt.% sodium is picked up by the mercury passing through the electrolyzer.

Diaphragm Cells

The diaphragm chloralkali cell is currently the principal means of producing chlorine and caustic in the United States and Canada.

During 1975, 73.4% of the operating United States chlorine capacity was in diaphragm cells, 21.8% in mercury cells, and 4.8% in all other production routes. In Canada, 64.6% of the chlorine capacity was from diaphragm cells and 35.4% in the mercury cell process. The diaphragm chloralkali cell is therefore the principal method for chlorine production in the United States and Canada.

Cell Operation

The diaphragm cell appears exceptionally simple on first principles from the standpoint of basic design and operation. Figure 3 shows the typical vertical electrode diaphragm-type cell design. In modern cell designs the cathode, on which asbestos is vacuum deposited to form the diaphragm, separates the main

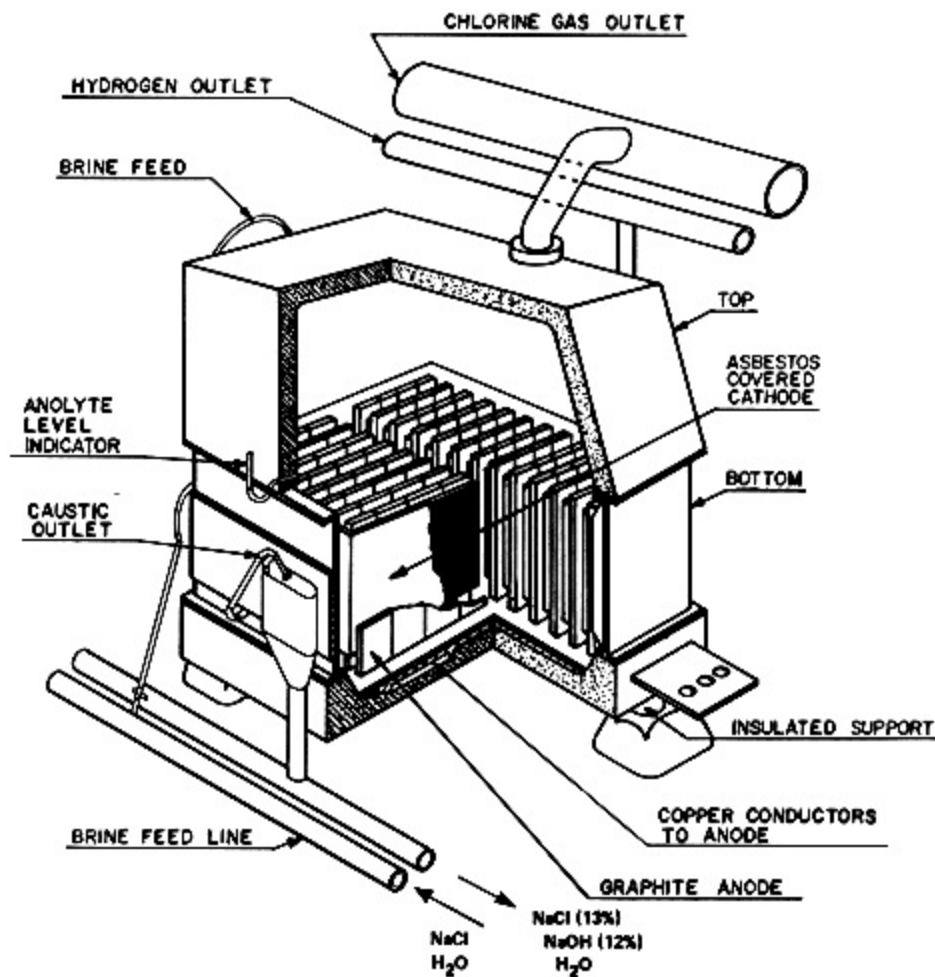


Fig. 3.

Diaphragm cell in cross section showing the metal anodes, diaphragms, and cathodes for use in chlorine and caustic production.

volume of the electrolyte into anolyte and catholyte, as seen in Fig. 4. Treated and purified brine enters the anode compartment and percolates as a bulk flow of brine through the diaphragm into the cathode chamber. This rate of percolation through the diaphragm is dependent on the height of the brine head level, as seen in Fig. 4. The rate of brine flow across the diaphragm is of necessity a compromise. A dynamic balance between the desired high concentration of caustic soda in the catholyte and the observed back-migration of hydroxyl ions from catholyte to anolyte develops because of the concentration gradient of electrolytes across the separator [6979].

Since the catholyte level and the resulting volume of the hydrogen disengaging space is controlled manually on these cells by setting the level of the percolating pipe, it develops that the highest electrical load demands the lowest normal setting of the catholyte level. The anolyte level is a function of the catholyte level and also depends on the condition of the diaphragm for a given feed rate and cell liquor composition.

In the diaphragm cell, direct current decomposes the salt in the brine to

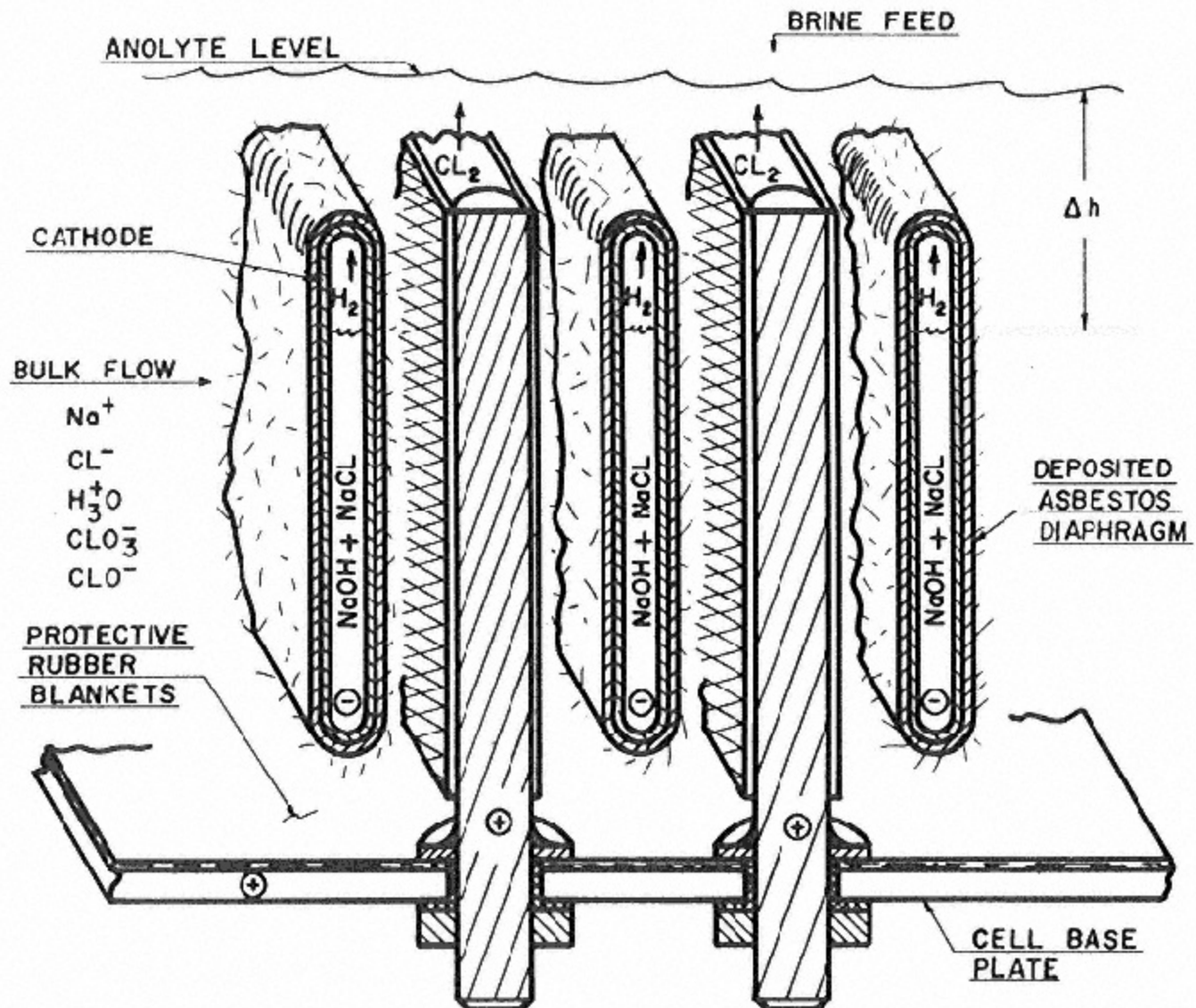


Fig. 4.

Oblique view of a typical chlorine-caustic diaphragm cell showing all essential ancillary equipment and fixtures. The catholyte

level and amount of hydrogen disengaging space is controlled manually by the setting of the percolating pipe. The highest cell load requires the lowest normal setting of the catholyte level. The anolyte level is a function of the catholyte level and of the condition of the diaphragm for a given brine feed rate and cell liquor composition.

produce chlorine at the anode and hydroxyl ions plus hydrogen at the cathode. In ideal cell operation, saturated brine of about 23% NaCl is decomposed to about 50% of its original concentration, as compared to 1020% depletion for mercury cells, with each pass through the electrolyzer. The electrical resistance within the cell generates heat that results in the cell operating temperature of 8590°C.

The electrolytic decomposition of brine forms oxygen, chlorine, and chlorine oxides at the anode. With metal anodes, the oxygen and chlorine discharge together, but with graphite anodes some of the oxygen produced reacts with the graphite electrode to form carbon dioxide. Because of these losses of graphite at the anode, the gap between electrodes increases. It is the wider gap along with a plugging of the diaphragm with graphite particles that increases the interelectrode resistance or IR drop during operation. The plugging of the diaphragm with graphite particles along with calcium and magnesium from the brine reduces its operation time on line to around 100200 d before the asbestos diaphragm must be replaced [71, 72].

Chlorine leaves the anode in a relatively pure form, except for the presence of small amounts of oxygen and carbon dioxide. Hydrogen is evolved in the cathode compartment as a gas and separated by the diaphragm from the chlorine. The catholyte solution, or cell liquor, contains 1116 wt.% caustic and 1611 wt.% salt along with 0.1 to 0.2% chlorate and hypochlorite. The liquor must be concentrated to about 50% for commercial use. Multiple effect evaporators are normally used (see Fig. 4).

The power consumption of typical Diamond MDC-20, 29, and 55 diaphragm cells is shown in Fig. 5 in terms of current density and cell voltage. The most typical cell operating current density is in the 1.52.5 kA/m² range. A 95% cathode current efficiency and 33.5 V requires 24002800 kWh/ton of power input for the chlorine produced. The cathode current efficiency depends directly on the caustic concentration. Figure 6, which shows the relationship of caustic strength and cathode current efficiency, indicates a 150 kA load or 1.5 kA/m² for a typical Hooker H4 cell. The caustic concentration must be kept below 150 g/l to give good electrolytic cell performance in terms of cathode current efficiency and chlorate produced. In order to produce the caustic in the commercial 50 wt.% range, however, the cell liquor of 12% must be evaporated [6774].

Caustic Evaporation

After the caustic reaches 50 wt.% during evaporation, the salt becomes insoluble in the caustic and can be removed to the 1% level by filtration or centrifugation [75]. Figure 7 shows a flow diagram for a mixed feed, triple effect caustic evaporator plant. The evaporation section of the plant requires even more capital investment than the electrolysis section because of its size and complexity and the cost of the materials used in its construction. Most of the process equipment that contacts the caustic must be made of nickel or high nickel alloy stainless steel for resistance to corrosion. High levels of chlorate in the cell liquor cause serious corrosion problems to this plant.

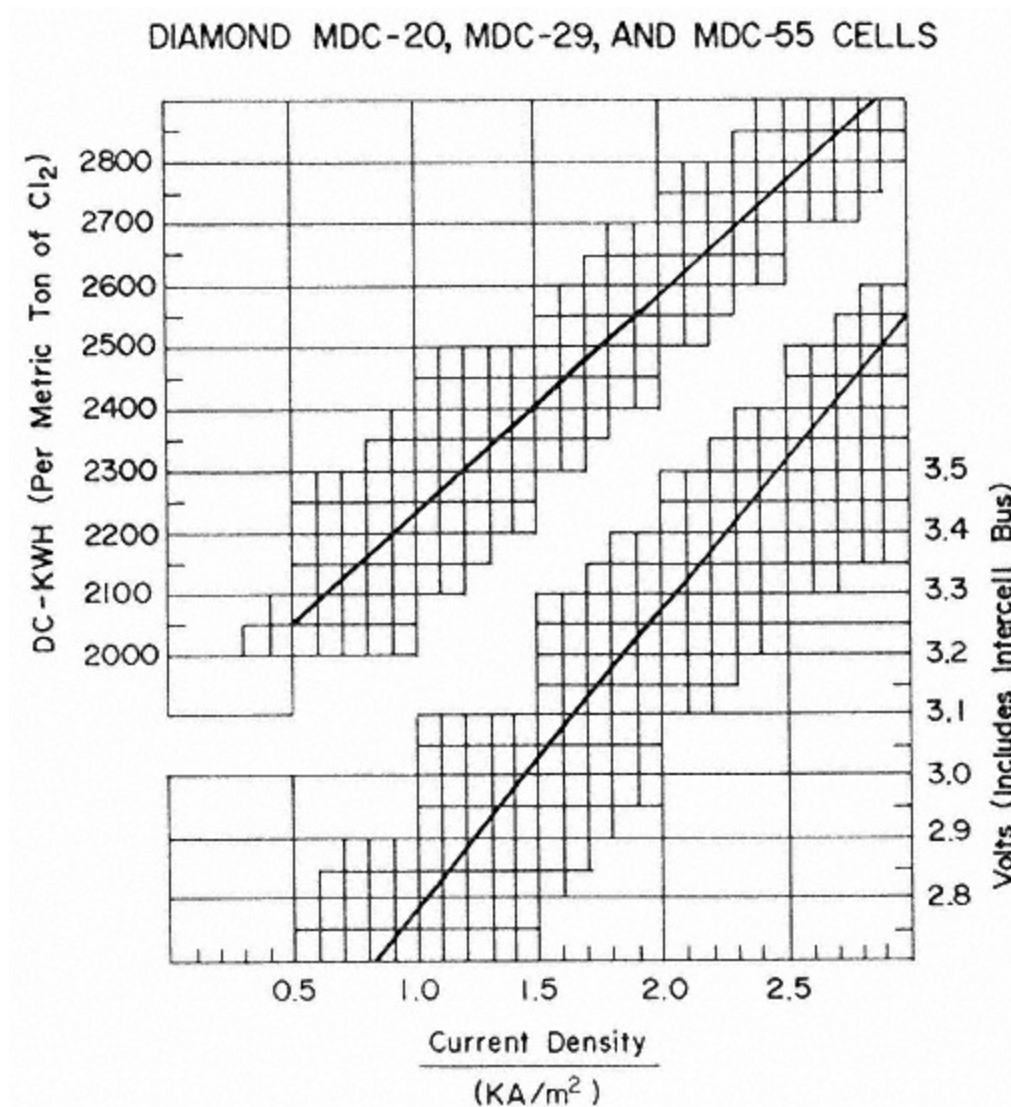


Fig. 5.
Power consumption for typical Diamond diaphragm cells.

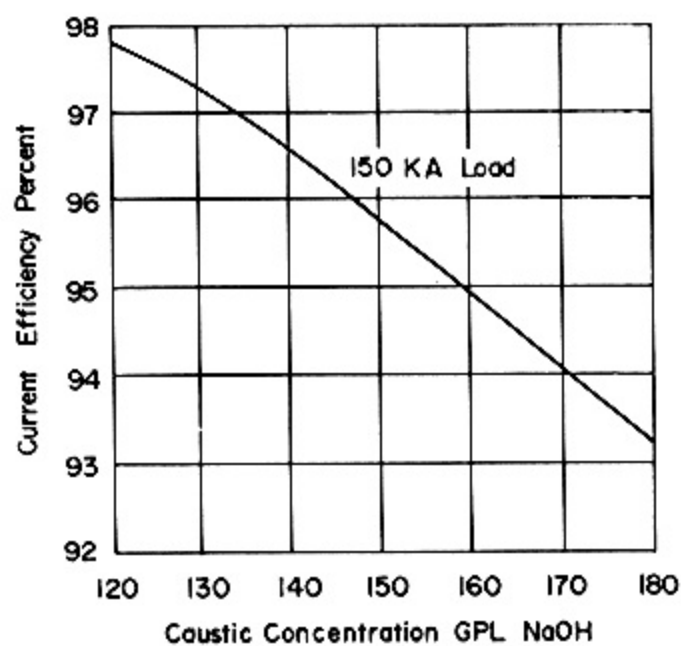


Fig. 6.
Current efficiency versus caustic concentration for a Hooker

diaphragm cell.

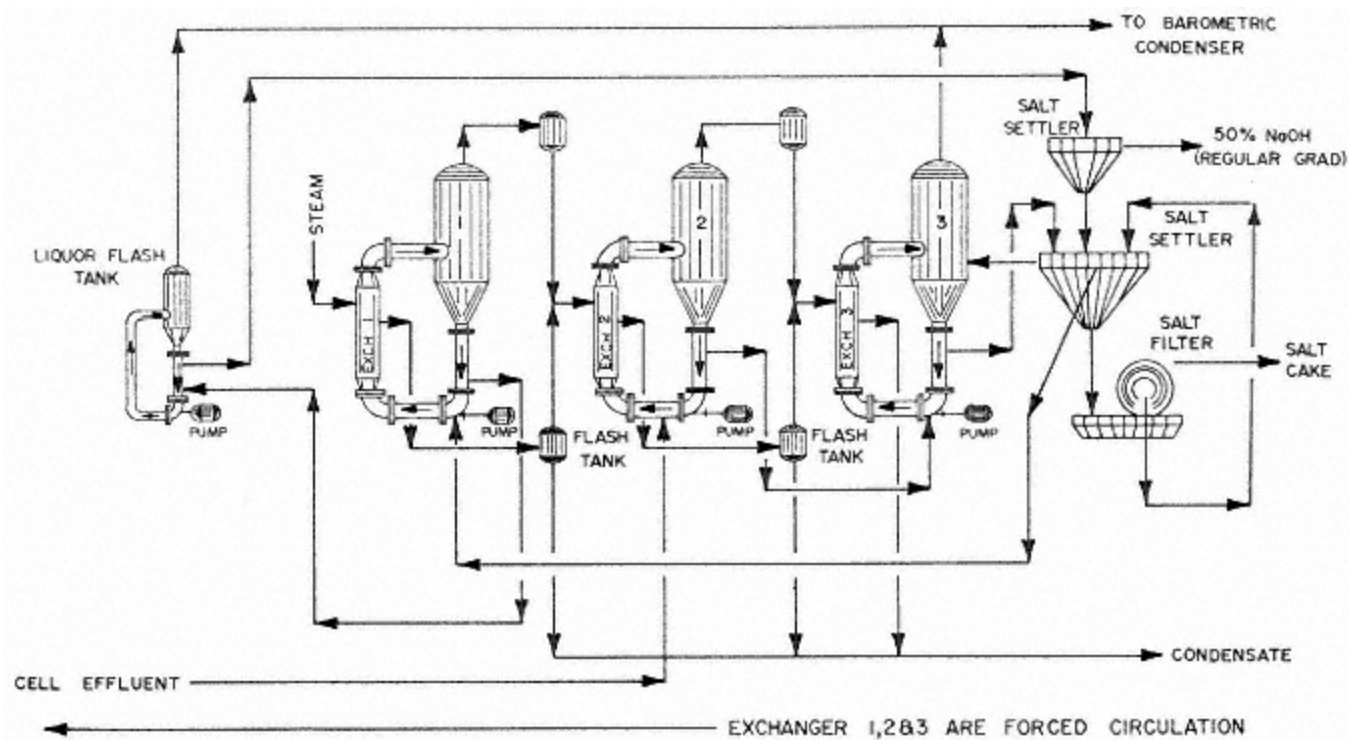


Fig. 7.
Flow diagram of a mixed feed triple effect caustic evaporator.

The cell liquor from the electrolyzer section is pumped initially into the second stage of the system and is concentrated from 16 to 25%, then to the third effect where it is concentrated to 38%. It is next pumped to the salt settler where salt is removed for the first time, and only then is it pumped to the first effect where it is evaporated to 50%, pumped to the liquid flash tank, then to the salt settler for salt removal to 1% or less, and finally transferred to the loading section for shipment. All of the heat exchangers on the first, second, and third effects are forced circulation [7577].

Energy Consumption

The overall consumption of energy for a diaphragm cell plant can be analyzed and balanced as shown in Figs. 8 and 9.

Figure 8 shows the energy balance for the electrolysis and gas pretreatment stages of production, while Fig. 9 shows the energy balance for the caustic evaporation process.

Figure 8 gives the typical energy input for a diaphragm cell as + 2590 kWh/ton; the endothermic heat of reaction is -1582.2 kWh/ton; the radiation and conduction losses are -644.6 kWh/ton; the hydrogen fuel credit-value is + 879 kWh/ton; losses to the cell liquor and caustic soda process are -293 kWh/ton; finally, losses in wet chlorine gas to cooling and drying are -58.6 kWh/ton. Input and output plus disappearance balance when the fuel value of hydrogen is omitted, because it is accounted for in the overall endothermic heat of reaction.

Figure 9 gives typical energy input for the caustic evaporation plant with an energy input of + 1465 kWh/ton and heat reflection of -29.3 kWh/ton due to radiation and convection, -1318.5 kWh/ton due to the formation of water vapor, and finally -118 kWh/ton due to formation of the primary product 50% caustic, based on an energy per unit weight of 100% caustic soda [78, 79].

Diaphragm cells and mercury cells have been competitive in the past, but environment and product quality problems have forced the rapid research and development of a third new kind of cell, the membrane cell.

Membrane Cells

During the past 8 years this third major type of cell has been invented and it has been developed from bench to pre-pilot, pilot, and finally to the commercial stage of plant operation in this time frame [8591].

These cells use metal anodes and perfluoroethylene-perfluorovinyl-ether ion exchange membranes with sulfonate and carboxylate functional groups attached. They operate for extended time periods with two chambered cell designs to produce high quality caustic and chlorine.

The instantaneous decision as to whether or not to install diaphragm or membrane cell

capacity at present depends mainly on the comparative costs of new and replacement capacity with respect to capital and operating costs.

The successful development of the membrane cell has been based on a good

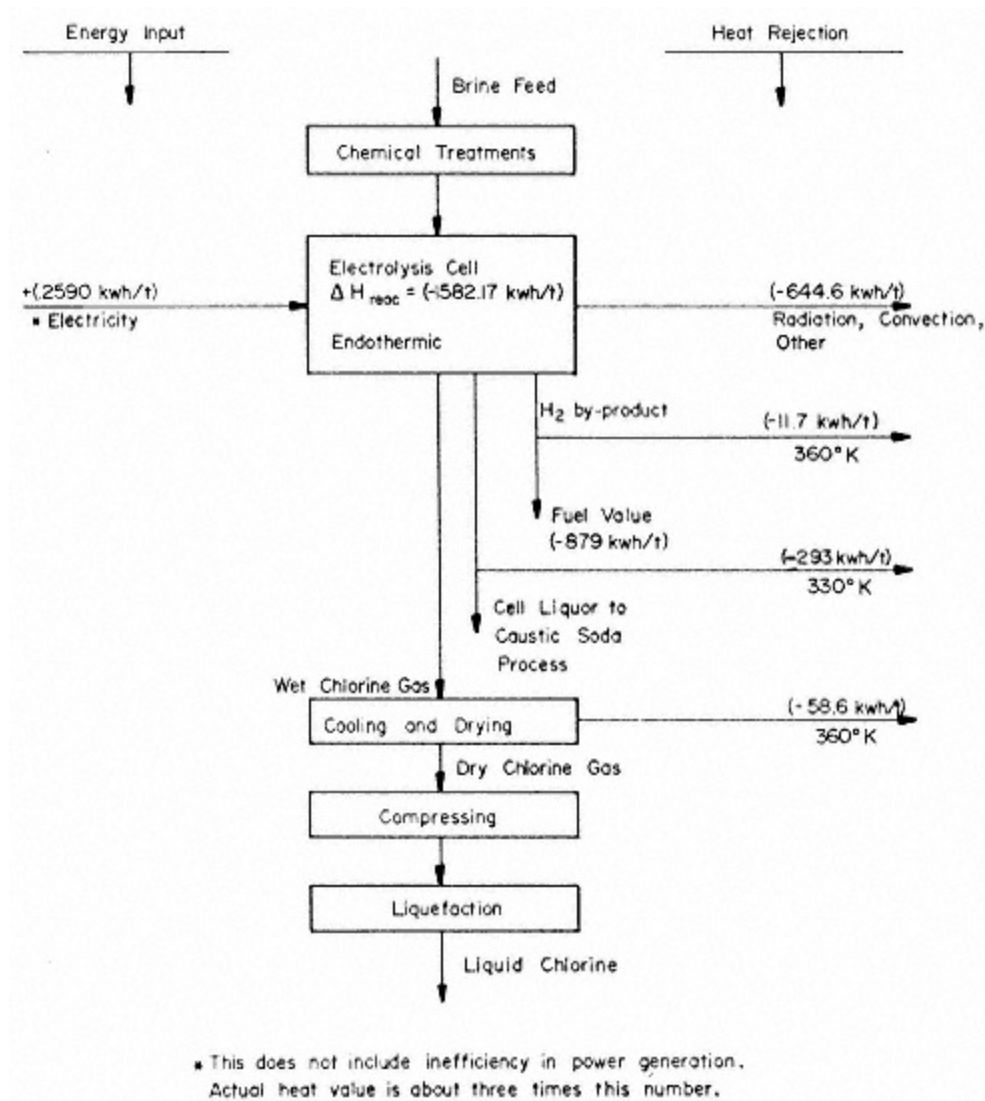


Fig. 8.

Chloralkali energy consumption diagram showing electrolytic section of a diaphragm cell plant.

membrane with structural integrity, dimensional stability, low resistance, and high current efficiencies over a long operating life in the cell.

One of the most important variables for commercial operation of membrane cells is the performance as a function of time. Since ion-exchange membranes are continuously variable and dynamic systems in most cases, it takes several days of continuously operation to reach steady state [8091].

Figures 10 and 11 show a type of monopolar membrane chloralkali cell using picture frame clamping of the separator in a tank-type design. Figure 11

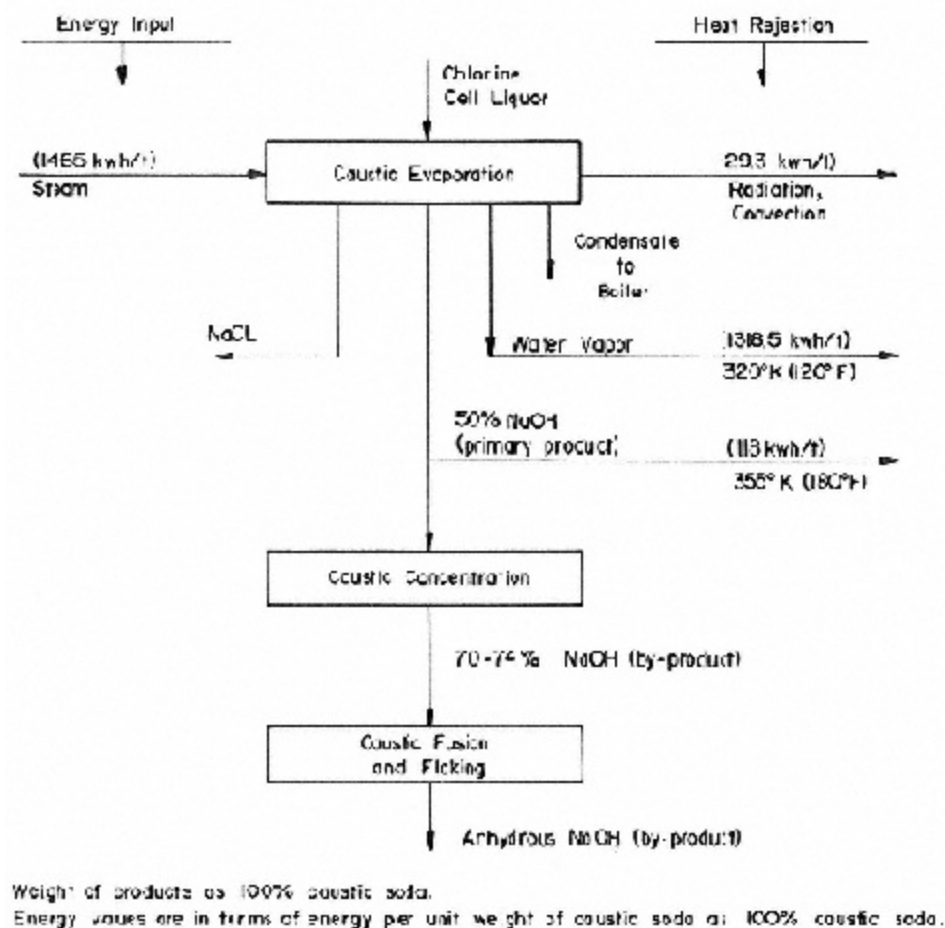


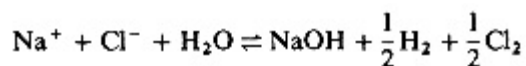
Fig. 9.

Chloralkali energy consumption diagram showing caustic evaporator section of a diaphragm cell plant.

shows the total cell tank along with the electrical connections assembled with the cell units.

Figure 12 shows a typical bipolar type of electrolyzer. It shows one cell in an exploded view for definition of the assembly conditions. Figure 12 also shows the assembled segments of the bipolar electrolyzer operating in a filter press system.

The electrode reactions for the diaphragm and membrane cells are the same:



Just as with diaphragm cells, the cathode current efficiency depends on two factors: (1) the amount of hydroxyl ion back-migration across the separator

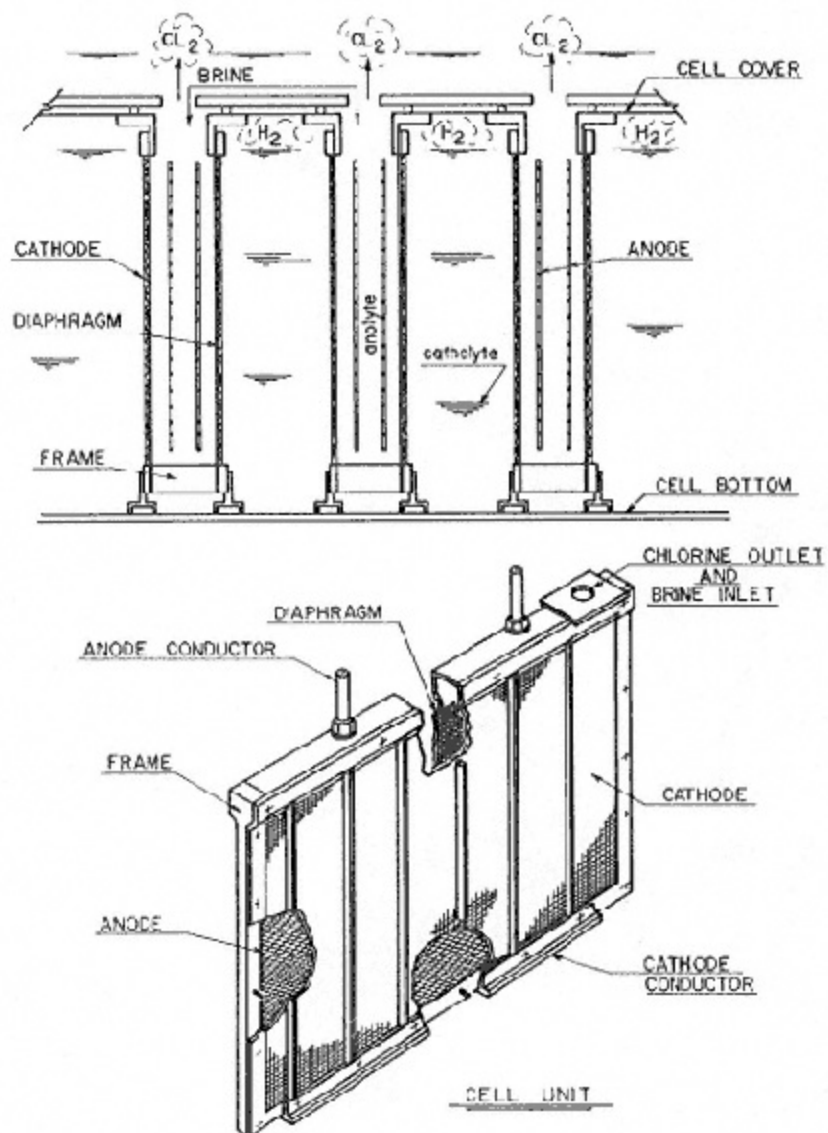


Fig. 10.
SK-type monopolar membrane chloralkali cell with picture frame clamping of separator in a tank-type design.

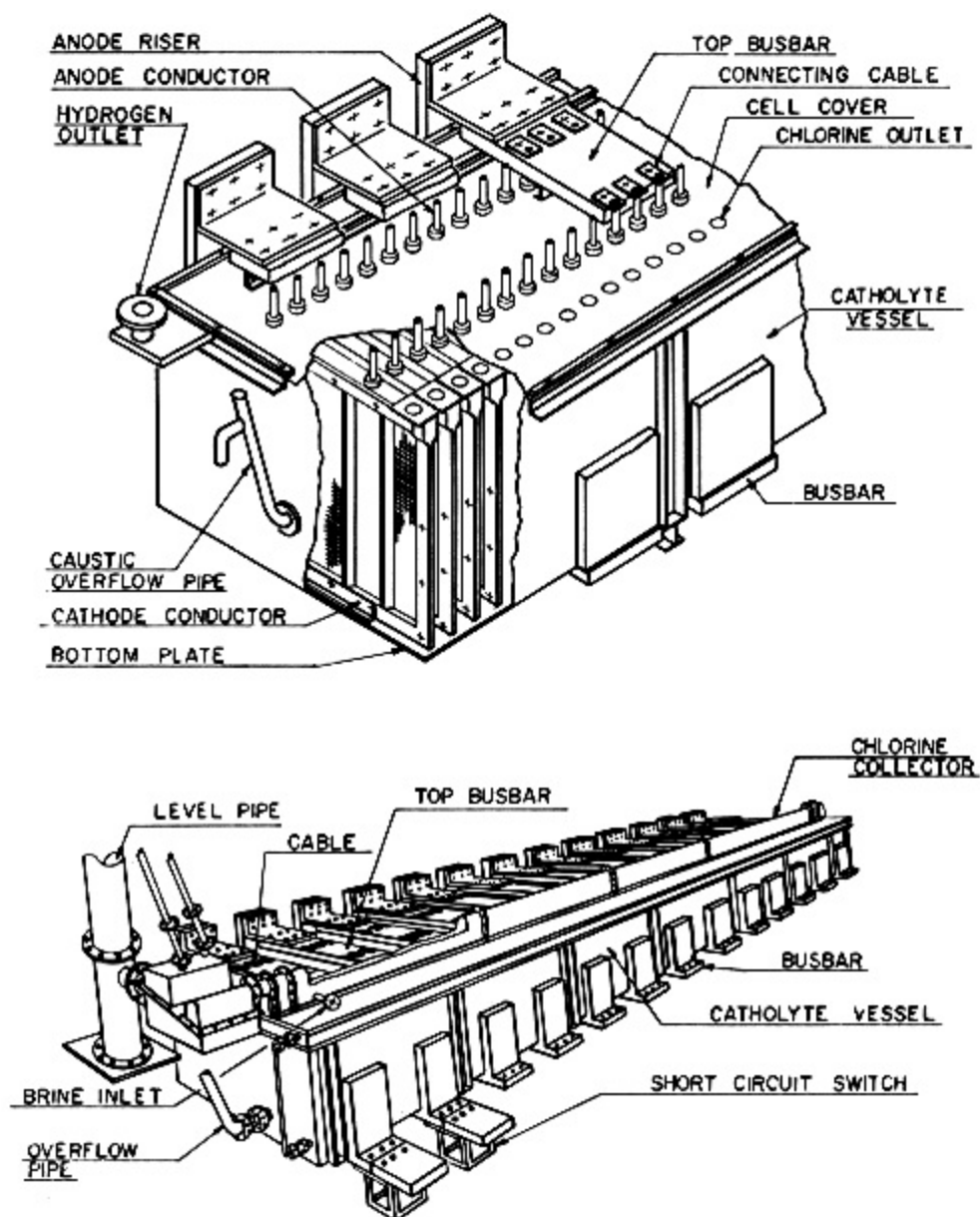


Fig. 11.
SK-type total cell tank and electrical connections assembled with cell units.

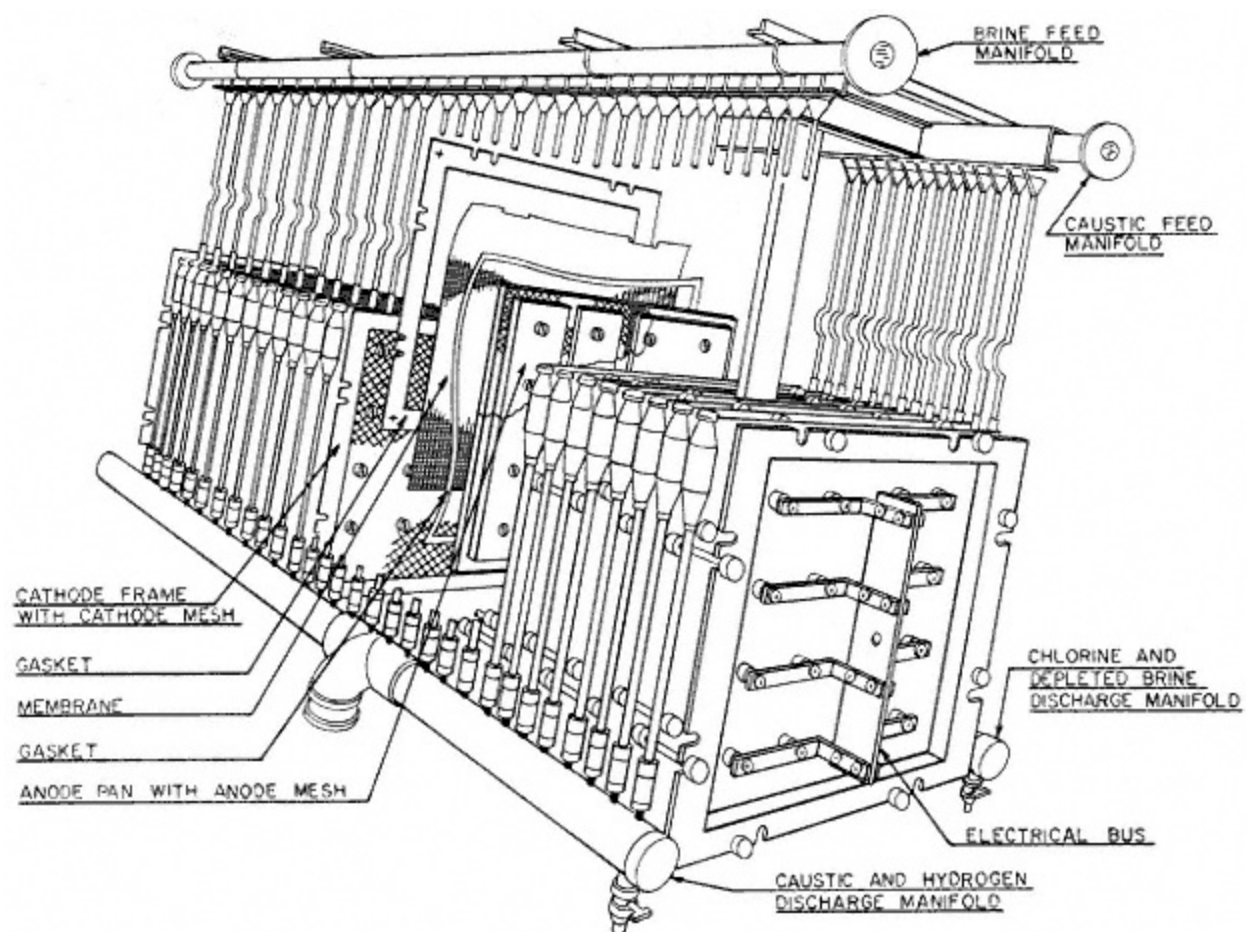


Fig. 12.
DB-10 type bipolar electrolyzer with one cell exploded for definition of assembly conditions.

from catholyte to anolyte, explicitly described as the ratio of Na^+ to OH^- fluxes; and (2) the extent of membrane polarization at the brine-membrane phase boundaries, depending on brine concentration [8591].

At present, the membrane-cell chloralkali process can compete with conventional mercury and diaphragm cell processes in plant sizes up to 500 tons/d chlorine production, and it will soon become competitive for all tonnages up to and including 1000 tons/d [9193].

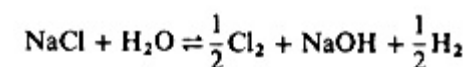
The use of permselective ion-exchange membranes in electrochemical chloralkali cell reactions, as first patented in the United States in the early 1970s, clearly represents a major innovation in electrochemical technology [8591].

Chlorate Cells

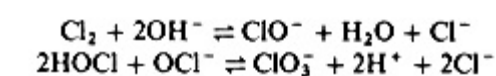
Chlorate cells usually have no separator to isolate anode cathode products, and are often fitted with cooling coils or heat exchangers to reduce the electrolysis and reaction temperature as shown in Fig. 13. The raw material is salt brine that has been purified to free it from heavy metals plus magnesium and calcium. These containments may form thick oxides as layers on the cathode to increase the cell resistance. Chromate is added to the electrolyte in order to regulate the acidity for giving rapid chlorate formation and at the same time passivate the iron or titanium portions of the cell to prevent hypochlorite reduction there [94].

The reactions involved in chlorate production are as follows:

Electrochemical:



Chemical:



In the preparation of chlorate, the electrolyte is recycled continuously. After saturation is reached the solution is allowed to crystallize at 750 g/l, and after this point is reached the solution is either evaporated or cooled to remove the NaCl which is then returned to the electrolysis cells [9597].

Some cell designs consist of a large cell body, with the volume of the electrodes only a small fraction of the total system. The cells, usually made of lined steel or polyvinyl chloride, are operated at 0.5 to 4.2 kA/m². Their temperatures usually run at 85 to 90°C, even though current efficiency improves as the temperature drops from 70 to 30°C with increased cell voltage. The current efficiency for potassium chlorate formation is over 90%, and for sodium chlorate over 80%.

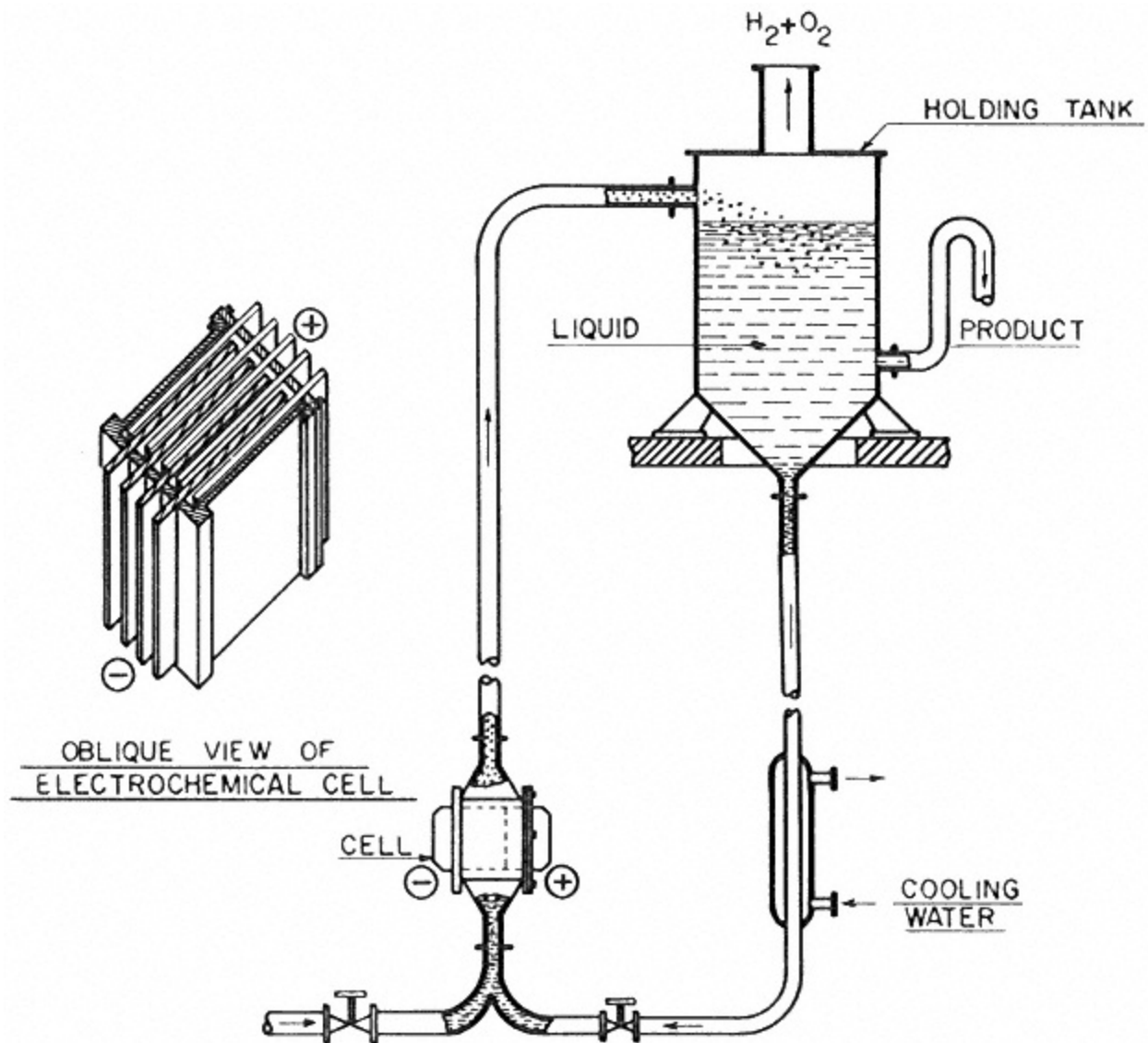


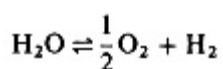
Fig. 13.

Chlorate cell system showing the electrochemical cell, reactor, and heat exchanger.

Water Electrolysis

Hydrogen and oxygen have been produced industrially by water electrolysis for over 75 years. Water is decomposed into its elements when a direct current passes through an aqueous acid or alkaline solution. The reversible decomposition voltage for water is 1.23 V, but practical cells operate at 1.8 to 2.6 V due to the overpotential and ohmic losses [98102].

The reaction in this case is



and 1000 A · h produces 0.43 m³ of hydrogen and 0.21 m³ of oxygen, and energy efficiencies of 45-65%. A typical tank-type electrolyzer is shown in Fig. 14. This picture shows the electrodes, diaphragms, gas collectors, and bus connections.

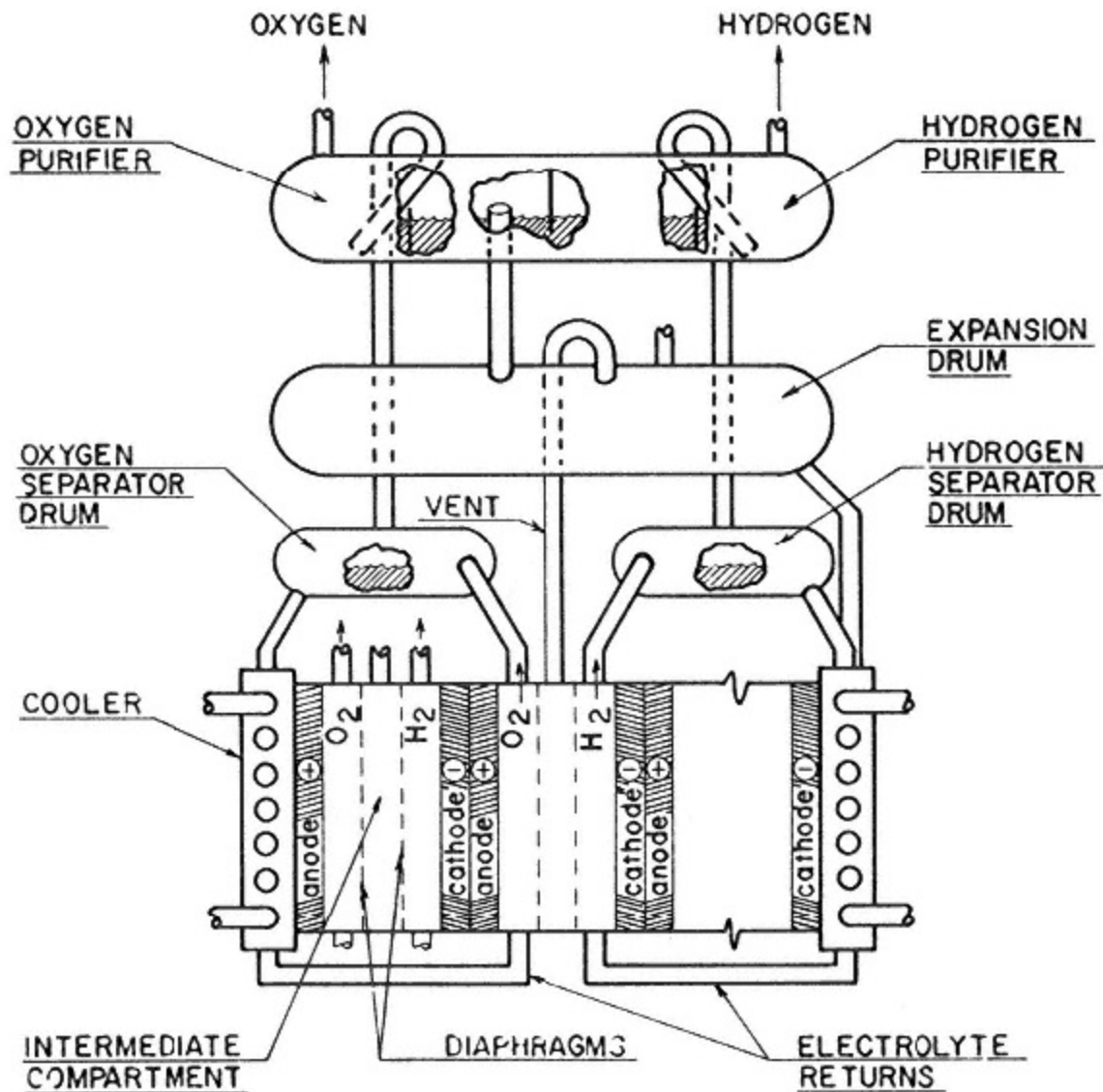


Fig. 14.
Filter press water electrolysis system.

Summary

In the electrochemical process industry, both process design and operation impact directly on reactor efficiency, capital, and operating costs.

From these discussions about the most prominent current aqueous electrochemical technology, it can be seen that the bulk mixing environment and overpotential of the electrodes in each reactor, or cell, affect its overall performance. It follows quite naturally that the electrochemical cells designed to operate with low concentrations of reactants require special provisions for the enhancement of mass transport of reactants to ensure efficient reaction at the electrode surfaces.

The most efficient and selective cells are hence those having the best defined and best controlled electrohydrodynamic conditions because, in the cell dispersion, mixing and transport processes couple with chemical reaction paths to affect reactor conversions.

A qualitative analysis of mass and charge transfer must be made quantitative through

bench studies and measurements on each reactor system for performance and life with each candidate process prior to scale-up. These studies are used to establish empirical correlations between the physical and

chemical characteristics of the cells and their electrochemical performance levels. This work is necessary for almost every system because of our present lack of general basic available information on kinetics, mechanistic, and transport processes, and this is why there is still no universally best reactor design for all systems.

Conclusions

Electrochemical science and engineering deal with ionics and electrodicts in a very practical way as they relate to the transfer of mass from one physical system to another, along with the transfer of charge from one phase to another, in order to establish the vital linkage between electrical and chemical energy forms. The understanding of these processes becomes more vital to our survival as energy conversions shift more and more toward electrical due to the effects of pollution, the diminishing supply of fossil fuels, and the availability of more low cost electrical power.

Effective research and development programs concentrating on energy supplies, energy conversion technology, and environmental clean-up are critical for a continued historical growth scenerio. We need to stop burning oil and gas as soon as possible in order to save these precious resources for nonenergy uses, i.e., fertilizers, petrochemicals, and plastics. Electric energy is the key because it is the only form in which atomic or hydroelectric power can be utilized industrially; however, at present we do not even understand how to most effectively generate, store, or consume it.

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Enzyme Processing

K. Venkatasubramanian

Biocatalysis represents a relatively new technique to the chemical processing industry. The term "biocatalysis" is used somewhat loosely here to include traditional fermentation processes and catalysis by isolated enzymes, cells, and subcellular particles in the free or immobilized forms. Fermentation processes in detail are covered by Humphrey [1]. The term "enzyme engineering" is often used to identify the latter subjects as a subtopic within the broad area of biochemical engineering.

Enzymes are biological catalysts which regulate the multitude of chemical reactions occurring in the living cell. They mediate such cellular processes as energy conversion, food digestion, and biosynthesis. Their practical application in fermented products such as cheese, bread, and alcoholic beverages dates back many centuries, long before the nature and function of enzymes, or even the microorganisms themselves, were known or understood. However, it was only in the beginning of this century that enzymes were shown to be the agents responsible for all fermentation processes.

In 1926 the first enzyme (urease) was crystallized. This established that enzymes are distinct chemical compounds with well-defined physical and chemical properties. Since then a great deal of knowledge on the structure and function of enzymes has been accumulated.

It is now recognized that all enzymes are proteins, made up of long chains of amino acids. The primary structure the sequence in which the amino acids are assembled has been worked out for a number of enzymes. The spatial architecture of an enzyme molecule greatly influences its catalytic function. The complete three-dimensional structures for several enzymes as well as methods to synthesize enzymes from amino acids have been established. Parallel to the investigations on the structure of enzymes, the kinetic and thermodynamic aspects of enzyme-catalyzed reactions have been studied equally ardently.

With the understanding of the nature of enzymes and their catalytic potency, industry began exploiting these versatile agents. Enzymes isolated from their parent organisms have had a long history of commercial use in the food and the pharmaceutical industries. Such isolated enzymes are often preferred over intact organisms containing the enzyme because the isolated enzymes act more specifically, their catalytic activity can be better controlled, and they are easier to handle and to store.

Enzymes offer a number of advantages as industrial catalysts over traditional inorganic catalysts. The high degree of substrate specificity largely eliminates the production of undesirable by-products and thus decreases the process costs and/or partial environmental burdens created by substitute nonbiological processes. Certain stereospecific reactions are quite complex when carried out without the aid of enzymes. Obviation of severe processing conditions substantially decreases the possibility of damage to heat-sensitive substrates and also reduces the energy requirements of the process. The implications of the resulting conservation of energy in the current context of escalating energy costs is obvious. Finally, the high reaction rates observed even under these mild operating conditions make the process more efficient and reduce the manufacturing cost. Thus the enzymatic processes may be designed to approach more nearly the ideal standard of efficiency embodied in the second law of thermodynamics.

In spite of these advantages, the use of enzymes in industrial applications has been limited to only a few food and drug products. First, the present cost of enzyme isolation

and purification is still high. Since the sources of most enzymes are the living cells of one form or another, their preparation is quite involved. Since each cell contains about 10002000

enzymes, large quantities of cell mass are required to obtain reasonable yields of the enzyme of interest. In addition, very delicate separation methods are required to release the enzyme undamaged from the cell and to isolate it from the cell remains. Second, most enzymes are unstable when removed from the living cell. Third, as many enzymes are employed in soluble form in dilute aqueous media, it is often difficult and economically prohibitive to recover them from reactor effluents at the end of the catalytic process. This restricts the use of soluble enzymes to disposable employment in essentially batch operations.

Immobilized Enzymes

A possible approach to circumvent these deleterious effects is to attach enzymes on to solid supports. This "immobilizes" the enzyme molecules and renders them insoluble in aqueous media. Some of the key advantages of immobilized enzymes over their soluble counterparts are summarized in Table 1.

From a practical standpoint, the term "immobilized enzyme" can be defined as a system or preparation in which an enzyme is confined or localized in a relatively defined region of space. The enzyme can be actually attached by one of several mechanisms to a supporting solid surface or it can be simply physically confined within a surrounding solid or liquid barrier. This is a rather loose definition of a catalyst system that can be easily separated from a reaction mixture, and can be used continuously in flow processes or repetitively in batch contacts as long as the enzyme preparation is active.

A few processes based on immobilized enzyme technology have already been reduced to industrial practice. In almost all these instances the key economic incentive is the dramatic reduction in enzyme cost achieved through the repeated use of the catalyst. Concurrent with this development, research and training in this new area of specialization Enzyme Engineering has become well established. In its broadest sense, enzyme engineering deals with the study of the production, isolation, purification, immobilization, and use of enzymes on the process scale.

It is clear that the heart of the fledgling enzyme technology is the immobilization of enzymes and the use of immobilized enzymes in efficient reactor systems.

TABLE 1 Advantages of Immobilized Enzymes over Soluble Enzymes

1. The enzymes can be reused
2. Continuous processes become practical
3. Improved stability of the enzymes; this is particularly true for proteolytic (protein-digesting) enzymes which can otherwise undergo autolysis
4. Greater purity of finished products
5. Enzyme activity is sometimes enhanced
6. Modified kinetic properties; can possibly be tailor-made for specific end-use
7. More favorable or broader environmental stability

Immobilized Microbial Cells and Organelles

Although the useful catalytic life of an enzyme is increased greatly upon immobilization, the problems of its isolation and purification (prior to immobilization) still constitute the most important factor in determining the overall economics of the bound enzyme system. Immobilization of whole microbial cells or organelles would eliminate these expensive steps, resulting in considerable improvement in process economics. The overall rationale for whole cell immobilization is outlined in Table 2.

The use of immobilized whole microbial cells and/or organelles eliminates the often tedious, time-consuming, and expensive steps involved in isolating and purifying intracellular enzymes. It also tends to improve the stability of the enzyme by retaining it in its natural surroundings during immobilization and subsequent continuous operation. Additional advantages may be realized when multi-enzyme systems and enzymes employing cofactors are immobilized within whole microbial cells. In the former case, purification steps for a number of enzymes are eliminated and methods to reconstruct the system in some optimum spatial arrangement are unnecessary. In the latter case, cofactor regeneration machinery included within the cell may obviate an external supply of such compounds. In addition, the enzyme and cofactor may already be arranged in some optimum way within the cell; thus, the possibility of retaining the structural integrity of the catalytic complex.

Immobilization of microbial cells mediating simple, monoenzyme reactions has already been translated into commercial scale. In contrast, the development of bound cell systems to carry out complex fermentation processes characterized by multiple reactions and complete reaction pathways involving coenzymes still in its infancy. However, the potential advantages of such an approach are enormous.

We have proposed the terms "controlled catalytic biomass" and "structured bed fermentation" to describe immobilized cell systems effecting such complex biocatalysis [2, 3]. The meaning of these terms is obvious when one considers the biocatalyst in relation to its microstructure, predesigned catalytic reactor design, and controlled catalytic activity vis-à-vis cellular reproduction.

This discussion is limited to immobilized enzyme and cell process systems rather than to the cultivation of microbial cells and/or isolation of

TABLE 2 Rationale for Whole Cell Immobilization

1. Obviates enzyme extraction/purification
2. Generally higher operational stability
3. Lower effective enzyme cost
4. High yield of enzyme activity on immobilization
5. Cofactor regeneration
6. Retention of structural and conformational integrity
7. Greater potential for multistep processes
8. Greater resistance to environmental perturbations

single enzymes from them. In particular, we shall discuss the materials science and the process engineering aspects of such bound systems and examine the current state of this technology. The first part of this article reviews the techniques of enzyme and cell immobilization and the second part discusses the properties of immobilized enzymes. The process engineering of bound enzyme and cell systems is considered in the final part. It should be added that the use of free enzymes in batch contacts represents but a rather trivial case of enzyme reactor systems.

General Considerations of Immobilized Enzyme Systems

There currently exist in the literature over 1500 reports concerning the immobilization and characterization of more than 200 different enzymes, most of which have appeared within the last 10 years. Well over 100 different supports have been used, and probably an equal number of specific immobilization techniques have been applied.

The many carriers that have been used are often broadly classified into two groups: organic and inorganic. Included among inorganic carriers are glass, alumina, clays, sand, colloidal silica, stainless steel, metal oxides, carbon, and ceramics. Representatives of organic supports are vinyl polymers, polysaccharides, proteins or polyamino acids, and polyamides. Other valuable subclassifications include natural or synthetic, neutral or polyelectrolyte, and porous or nonporous materials.

Despite the tremendous activity in the field during the last decade, there are few comparative studies aimed at making a critical appraisal of the many different techniques available for preparing immobilized enzymes. In fact, much of the research to date has primarily concerned itself with quick exploration of new methods and supports. The result is that the vast amount of data that have been accumulated, with its lack of cogency and even its apparent inconsistencies, could quite possibly lead to confusion among those seeking to use the developed technology. To complicate matters even further, there appears to be no single optimal method or universal carrier. In fact, the "best" system may vary considerably depending on the requirements of each different enzyme and on the specific conditions needed for a particular application, whether it be for industrial, medical, or analytical use.

Until recently there was no single publication which could serve as an integrated information source to those interested in the application of immobilized enzyme technology. There are, however, a number of excellent reviews which provide a comprehensive compilation of data related to various aspects of the field over given periods in its development [410]. In addition, several conference or symposia proceedings have provided summaries of a variety of important research efforts as well as guidelines and suggestions which were developed by attendees through workshop or other mechanisms [1117]. Three important works have been published within the past few years which serve as good single-source compendia of all basic aspects of immobilized enzyme technology [1820].

Techniques of Enzyme and Whole Cell Immobilization

The catalytic activity of an enzyme resides in its "active site" the locus at which the substrate molecule is bound to the enzyme and converted by it. The active site usually consists of several amino acids held in a specific spatial relationship to each other. The three-dimensional conformational structure (tertiary structure) of the enzyme is also critical in the overall catalytic action. Consequently, for the expression of enzymatic activity by the immobilized enzyme, it is necessary to retain the same structural state without altering the amino acid residues at the active center or affecting its tertiary structure. For this reason, enzyme immobilization methods require extremely precise conditions. Further, it is necessary to carry out the immobilization reaction under very mild conditions. High temperature reactions, acid/alkali treatments, high salt concentrations, etc., should be avoided to preserve the structural integrity of the enzyme.

Over the past few years a number of techniques to immobilize enzymes on solid matrices have been developed. Here we shall briefly highlight the salient features of these methods. Enzyme immobilization methods have been classified under four basic categories. However, for some cases, the method used is a combination of two or more of these categories.

1. Adsorption at a solid surface
2. Trapping in a gel
3. Cross-linking by means of bifunctional reagents (often in combination with 1 or 2)
4. Covalent binding

Enzymes Immobilized by Adsorption

The simplest way to immobilize enzymes is by adsorption by simple exposure of the solid surface to the enzyme solution under very mild conditions. However, the binding forces between the enzyme and the carrier are weak; therefore the enzyme can be desorbed easily in the presence of substrate or concentrated solutions of electrolyte. Further, the nonspecific adsorption process might lead to partial or total denaturation of the enzyme. A carrier would be suitable as an adsorbent only when it possesses high affinity for the enzyme and, at the same time, causes minimal denaturation.

Both charged and neutral supports have been used for the adsorption of enzymes. Ion-exchange resins such as DEAE-Sephadex, DEAE-Cellulose, and carboxy methyl cellulose have been particularly popular. An immobilized enzyme process employing aminoacylase ionically bound to DEAE-Cellulose is being used on an industrial scale in Japan [21, 22]. Glass, quartz, bentonite, charcoal particles, and silica gel have also found use as adsorbing carrier matrices. One way of improving the retention of adsorbed enzymes within the support matrix is through intermolecular cross-linking by means of bifunctional agents such as glutaraldehyde.

Physical Entrapment in Gel Lattices

Polymeric gels provide semipermeable physical barriers to the escape of enzymes while allowing the passage of the substrate and the product. Enzymes and whole cells can thus be occluded within a cross-linked gel matrix. The entrapment of enzymes is generally carried out by polymerizing an aqueous solution containing the carrier (in the monomeric form) and the enzyme in the presence of a cross-linking agent. Polyacrylamide and starch gels have found wide usage for immobilizing not only different enzymes but also whole microbial cells.

Enzyme or whole cell immobilization via physical entrapment offers the advantage of relatively mild reaction conditions without significant alteration of the enzyme. Also, this method has a general applicability to different enzymes. The major drawbacks of this mode of enzyme immobilization are (1) the continuous leakage of the occluded enzyme because of the large distribution of pore sizes, and (2) the large diffusional barriers to the transport of substrate and product, more so in the case of high molecular weight substrates.

A variation of the entrapment method is to form microcapsules containing enzymes. Thin spherical semipermeable nylon or collodion membranes shaped into microcapsules have been used to immobilize different enzymes. Another version of this technique employs hydrophobic liquid membranes to achieve semi-permeability.

Covalent Binding

The widely studied covalent linkage of an enzyme to a carrier is accomplished through functional groups on the enzyme which are not essential for its catalytic activity. Included among such functional groups are (1) the free amino and carboxyl groups, (2) the hydroxyl group of serine and threonine, (3) the phenolic group of tyrosine, (4) the imidazole group of histidine, and (5) the sulfhydryl group of cysteine. The coupling reaction should obviously be carried out under mild conditions to minimize the possibilities of enzyme denaturation.

The covalent coupling reactions employed for the binding of the enzyme onto the carrier fall under three major categories: (1) linkage through the formation of a peptide bond, (2) attachment through alkylation, and (3) diazo linkage. The formation of a peptide bond between either the ϵ -amino group or the N-terminal amino group and the carrier is accomplished through agents like cyanogen bromide. The carrier carboxyls can also be activated by means of carbodiimides by Woodward's reagent or by their transformation into corresponding azides.

By using carriers possessing a functional group such as a halogen, alkylation of the free amino groups, the phenolic group of tyrosine, or the sulfhydryl group of cysteine can be accomplished. The attachment of enzymes to cellulose by using cyanuric chloride is an example of this technique. The diazo coupling route involves the preparation of an inter-

mediate polydiazonium salt of the carrier and reacting it with the enzyme under appropriate conditions to bind the enzyme. Enzymes possessing free tyrosine residues can thus be linked to different carriers via azo bonds. Inorganic supports like porous glass can be activated by coupling with γ -amino propyl triethoxysilane and the resulting derivative can be converted to the isothiocyanate derivative or it can be diazotized.

Immobilization by Intermolecular Cross-Linking

By using bifunctional reagents to induce intermolecular cross-linking, enzymes and whole cells can be bound to solid supports. Glutaraldehyde, bisdiazobenzidine-2,2'-disulfonic acid, toluene-2-isocyanate-4-isothiocyanate, trichloro-S-triazine, etc., have been employed as the cross-linking agents.

Immobilization of enzymes through covalent binding or by intermolecular cross-linking eliminates some of the difficulties associated with the other modes of immobilization. Conversely, covalent attachment alters the chemistry of the enzymes and may change its reactivity. In some cases the active site of the enzyme may be affected by the coupling reaction, leading to the loss of enzymatic activity.

Summary

Table 3 summarizes the relative advantages and disadvantages of the different techniques of enzyme immobilization. Even a cursory glance at this table suffices to reveal that none of these techniques has a clear edge over the others. Even though there is no dearth of available techniques, the main question is how many can realistically be carried beyond the laboratory stage. For eventual adaption into industrial practice, the immobilization procedure should be simple, inexpensive, have a general applicability to a variety of enzymes, and be capable of ready scaling-up. An effective approach to meeting these requirements would be to develop methods which would combine the advantageous features of all these techniques while minimizing their disadvantages. A few techniques already sealed-up to industrial processing have focused their attention in this direction.

Two examples of such an approach are included here. The first one, developed by Imperial Chemical Industries, involves bound cells of *Arthrobacter* Sp. for the conversion of glucose to fructose (glucose isomerase enzyme activity). In this case the cells are flocculated with the aid of polymeric coagulating agents, followed by extrusion and drying (Fig. 1). The simplicity of this process from a large-scale operational

TABLE 3 Comparison of Different Immobilization Techniques

Characteristics	Adsorption	Entrapment	Covalent Binding	Cross-Linking
Preparation	Simple	Difficult	Difficult	Difficult
Binding force	Weak	Weak	Strong	Strong
Enzyme activity	Low	Low	High	Low
Regeneration of the carrier	Possible	Impossible	Impossible	Impossible
Cost of immobilization	Low	Moderate	High	Moderate
General applicability to different enzymes	Yes	Yes	No	No

^aIn the case of ionic-binding to ion-exchange resins such as DEAE-cellulose, higher enzyme activities have been reported.

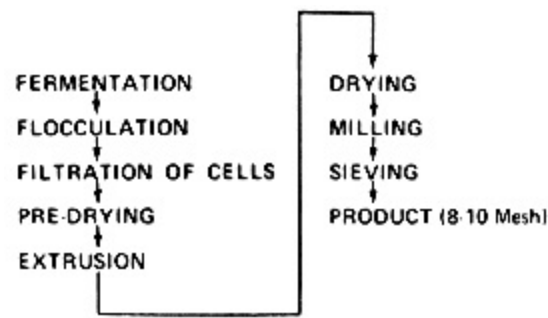


Fig. 1.
A commercial process for immobilization of microbial cells.

viewpoint is worth noting. The second example relates to the immobilization of different enzymes, cells, and organelles on a biological protein, viz., collagen. Much effort has been expended over the past decade to develop this technology which is now being evaluated on a pilot-plant scale in industry. Many reviews of this work have already appeared in the literature [8, 23].

Criteria for Choice of Carriers and Immobilization Techniques

It is difficult to present a single list of criteria for choosing a particular carrier and immobilization technique since the "best" choice depends on the enzyme and on the type of application in which it is to be utilized. Goldstein and Manecke [24] provide an excellent example of how difficult it is to predict the performance of a certain carrier and technique based on results with other enzymes. Similarly, characteristics can vary substantially for the same enzyme bound to different carriers or to a single carrier by different techniques. One of the most exhaustive studies which demonstrates this point is that involving aminoacylase as reported by Chibata and Tosa [25].

Despite the large variation that can be expected in the performance of a particular carrier and immobilization method, depending on the enzyme and on the type of application, it is useful to define parameters of immobilized enzyme systems which can be used for their characterization and evaluation [1820]. Some of the more important parameters as they relate specifically to industrial processing are listed below.

Activity

One of the more important characteristics of an immobilized enzyme preparation is its expressed activity. The catalytic activities are often

presented as initial rates in terms of international units (μ moles substrate converted per minute) per gram or unit surface area of the catalyst. For some enzymes a "unit" may have a special definition. The expressed activities of immobilized enzymes are very dependent on environmental conditions such as initial substrate concentrations, effector concentrations, temperature, pH, reaction time, ionic strength, buffer concentration, agitation or flow rate, and physical dimensions of the carrier. These conditions should always be presented with activity data, a practice which has all too often been overlooked in the literature.

Bound Protein

Since activity measurements are so sensitive to assay conditions, some authors feel that the amount of protein bound to the carrier is a better method of characterizing the effectiveness of a particular immobilization technique. The amount of bound protein is also important when investigating the kinetic behavior of the complex. Unfortunately, these data, which are usually presented as milligrams of protein per gram of carrier, are much more difficult to obtain than activity measurements.

Specific Activity of Bound Protein

This parameter ("units"/mg bound protein) can be determined from the expressed activity of the preparation and the amount of bound protein. Like the total activity of the complex, it is extremely dependent upon the environmental conditions of the assay. A comparison between this parameter and the specific activity of the soluble enzyme provides some idea of the effectiveness of the immobilization procedure.

Coupling Yield

There are a number of ways of characterizing the amount of enzyme successfully bound to a carrier compared to the amount initially applied in the immobilization procedure. Broun [26] defines the following parameter:

$$\rho (\%) = \frac{\text{overall activity of insolubilized enzyme} \times 100}{\text{overall activity of the initial enzyme solution}} \quad (1)$$

where ρ is the "activity yield." For methods where the initial enzyme solution can be reused, the denominator might be modified by subtracting the amount of soluble enzyme recovered after completion of the immobilization step. Similar parameters can be defined based on the percentage of applied protein that is successfully bound to the carrier. Activity yield is generally the more important parameter from a process

design standpoint since the bound protein may be inactive or inaccessible to substrate.

Stability of Carrier-Enzyme Complexes

The stability of an immobilized enzyme preparation can be characterized in several different ways. One method is to determine the shelf-life or "storage stability" of the preparation. A much more valuable characteristic, however, is the so-called "operational stability" of the system. This parameter is determined by monitoring the activity of the immobilized enzyme during continuous use under the environmental conditions that the system will encounter in its ultimate application. Ideally, these data should be obtained using actual industrial substrate streams, actual flow rates, and so on. In most cases, operational stability data are presented as activity half-lives.

Materials, Methods, and Conditions of Binding Technique

Although each binding technique will be evaluated by the properties of the resulting conjugate, there are a number of characteristics of the methodology itself which are important to consider in an overall evaluation of the system. For an industrial application an important parameter is the cost involved in producing a complex with a given amount of stable enzymatic activity. Therefore, it is necessary to consider the expense of the required reagents and the need for specialized equipment as well as energy, labor, and maintenance costs involved in providing a continuous supply of catalyst for the process. An important consideration here may be the regenerability of the carrier matrix, i.e., the reversibility of attachment between enzyme and carrier.

In fact, the ability to regenerate aminoacylase-DEAE-Sephadex columns was a key factor in choosing that binding technique over covalent or entrapment methods in the design of a commercial process for continuous production of L-amino acids [25].

Another consideration that may affect the choice of a particular binding technique for a specific enzyme is a description of the environmental conditions to which the soluble enzyme must be exposed during immobilization. For example, some enzymes may be irreversibly denatured or inactivated in the presence of certain cross-linking agents or solvents while others tolerate the conditions well. Also important are the number of links formed between a bound enzyme and its carrier. While multipoint attachment should improve the operational stability of a carrier-enzyme complex, too many linkages per molecule may negatively affect the physical-chemical properties of the enzyme, such as its resistance to thermal denaturation. Unfortunately, few studies have been conducted to assess directly the number of links between carrier and enzyme.

Finally, the amount of protein bound by a particular procedure can have a great influence on the overall efficiency of the method. For a given

carrier the amount of bound protein can often be affected by the concentration of soluble enzyme used in the preparation. Although higher enzyme concentrations can lead to greater amounts of bound protein, lower concentrations usually improve activity yields, i.e., enzyme activity is more effectively utilized. Optimization of bound activity as a function of the soluble enzyme concentration applied to the carrier is therefore a useful study to conduct when evaluating the overall performance of a particular method.

Physical-Chemical Characteristics of the Carrier

The characteristics of the carrier material can influence the success or failure of an immobilized enzyme in a specific application. First of all, cost and availability of the material can affect the overall economics of the process, especially in applications using relatively inexpensive enzymes. For expensive enzymes, the overall cost of the process may not be so sensitive to carrier costs. Other characteristics of the carrier material which have a direct effect on process economics are its stability against physical, chemical, thermal, and microbial degradation; its mechanical strength and dimensional stability to avoid compaction and large pressure drops in flow processes; and its regenerability to avoid disposal problems. Related characteristics are the form or shape of the carrier matrix, its surface-to-volume ratio, and the concentration of binding sites, all of which have a direct effect on reactor size and geometry.

In addition to the direct effects discussed above, a carrier material can influence indirectly the performance and overall economics of an immobilized enzyme system. Sometimes a particular characteristic can have opposing effects which will necessitate some compromise or optimization in choosing the "best" carrier system. For example, porous carriers often provide a relatively large surface area which allows a high level of enzyme binding, but the porous structure also creates diffusional resistances to substrate and product transport which tend to reduce the expressed activity of the complex. In addition, a high concentration of binding sites on the carrier generally increases the total amount of bound protein, but the specific activity of the bound enzyme tends to decrease with increasing protein content in the complex. This phenomenon, which is often observed, could be a reflection of multiple linkages or increased mass transfer effects due to the increased activity of the preparation.

Important characteristics of the carrier are listed in Table 4. There is also some indication that proteinaceous supports are particularly effective in conferring enhanced stability characteristics [23, 26].

Immobilized Coenzymes

Some of the more dramatic applications of enzyme technology will occur when more complicated cofactors requiring enzymes are utilized. An important group of cofactors are the stoichiometric coenzymes such as

TABLE 4 Factors Influencing the Choice of Carrier Matrices

A. Factors which affect the binding capacity (amount of enzyme immobilized per unit weight of carrier):

- Bulk or surface density of binding sites

- Porosity

- Electrostatic charge distribution

- Hydrophile/hydrophobe ratio

B. Factors which affect the expression of enzymatic activity by the bound enzyme:

- Characteristic size of immobilized enzyme

- Form/shape of the carrier

- Charge distribution

- Diffusional resistances to substrate and product transport

- Reactor flow distribution

C. Other factors:

- Regenerability of the carrier

- Ease of enzyme attachment

- Operational stability

- Cost

NADH and NADP (see Symbols section). ATP, ADP, AMP, and coenzyme A actually act as cosubstrates in that their activity must be regenerated after involvement in the enzyme reaction. The use of these coenzymes in practical applications has been limited by at least three problems: (1) the coenzyme must retain its diffusibility since it acts as a group carrier, (2) the coenzyme must be maintained within the system in order to prevent the continuous requirement of an expensive compound, and (3) it must be regenerated within the reactor system in order to reuse a given amount of coenzyme continuously. Bright [27] and Mosbach et al. [28] have discussed several possible solutions to these problems and have provided reviews of some actual experimental systems.

Immobilized Multienzyme Systems

The immobilization on the same carrier matrix of two or more enzymes that catalyze sequential sets of reactions has generated considerable interest both from the standpoint of representing actual in vivo multienzyme systems and also for the development of practical processes. Although the basic carriers and immobilization techniques are no different than for single enzymes, there are a number of important considerations that are unique to multienzyme systems. For example, an extremely important parameter is the molar ratio of the enzymes on the carrier matrix. Other important considerations are the relationship between the molar ratio of enzymes, the mass transfer resistances in the reactor, and conversion to the final product. Several such features of multienzyme systems have been reviewed recently [29, 30]. Some immediate potential applications of mul-

tienzymes include conversion of starch to maltose and production of gluconic acid from glucose.

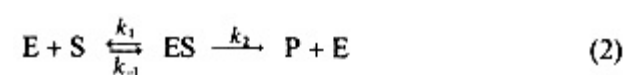
Appraisal of Immobilization Methods

An examination of experimental data for existing immobilized enzyme preparations suggests some very crude guidelines for appraising a given system. The "better" systems, in general, provide expressed activities in the range of 100 to 10,000 I.U./g of carrier, usually in the lower portion of this range. Protein binding capacities have been tabulated by Goldstein and Manecke [24] for several different carriers and immobilization methods. From their list, it appears that approximately 50 to 1500 mg protein/g conjugate is a reasonable range to expect for the better systems. The expressed activity of the bound enzyme is a more important parameter. The tabulation of Goldstein and Manecke indicates that covalent binding to copolymers formed from hydrophilic monomers and styrene derivatives appears to offer the highest binding capacities, especially when the conjugate is in macroreticular form. Operational half-lives of several weeks or months should be expected, especially for industrial applications. This characteristic and the expressed activity are probably the two most important parameters for reactor design. Taken together, they define the overall productivity of the catalyst, i.e., amount of product produced by a unit amount of catalyst over its entire useful life. Coupling yields can also be an important factor in the overall economics of the process, especially for expensive enzymes. In general, 40-80% may be considered "good" values, although lower levels may be acceptable, depending on the individual system. Yields of greater than 80% are considered outstanding.

Even with the above guidelines it is impossible to list the best carriers and binding methods without knowing something about the ultimate application. Certainly, there is no universal carrier or technique that can be applied automatically. Choosing an immobilized enzyme system for a specific application is still essentially empirical. Different methods are tested and characterized by the properties discussed in the following section. Since no single system will be perfect, the choice will depend on a careful consideration of the advantages of each system in the specific application. The data and experience generated so far may help narrow the choices, but in the end a trial-and-error approach is still required.

Kinetic Behavior of Immobilized Enzyme Systems

In the simplest model, the enzyme catalyzed reaction effecting the conversion of substrate S to product P may be presented by



where k_1 , k_{-1} , and k_2 are kinetic constants. Assuming that a steady state exists in which the concentration of the intermediate $[ES]$ does not vary with time, the following kinetic expression known popularly as the Michaelis-Menten relationship can be developed.

$$V = \frac{k_2 E_0 S}{K_m + S} \quad (3)$$

where V = reaction velocity of the enzyme
 V_{reaction}

K_m = Michaelis-Menten constant = $(k_{-1} + k_2)/k_1$

E_0 = total enzyme concentration

S = substrate concentration

When the concentration of the substrate is much larger than K_m , then $V = k_2 E_0 = V_m$ and the reaction rate is at its maximum. K_m is the substrate concentration at which the reaction velocity is half the maximal value. More detailed discussion of the kinetics of enzymatic reactions can be found in biochemistry texts.

When an enzyme is attached to a solid support, the kinetic pattern of the enzyme-catalyzed reaction changes considerably, leading to changes in the values of the kinetic parameters K_m and V_m . The kinetics of such reactions are obscured by several factors, and the observed kinetic parameters are only "apparent."

As mentioned earlier, the expressed activity and kinetic parameters of an immobilized enzyme are highly dependent on such factors as the physical dimensions and chemical nature of the carrier; the mixing or flow characteristics in the reaction system; and the concentrations of substrates, products, and effectors in the surrounding solution or macroenvironment. As such, these properties have often been labeled as "apparent" parameters since their value depends so strongly on reaction conditions. Unfortunately, "apparent" rate parameters are of little value unless there is some knowledge and understanding of how they are affected by important environmental variables. During the past few years a considerable effort has been directed toward the understanding and modeling of the heterogeneous nature of immobilized enzyme catalysts in order to improve the analysis and the use of rate data from these systems. Excellent recent reviews of these studies are available in the literature [19, 20]. Although some experimental data describing these effects are available in the literature, the major developments have thus far been primarily of a theoretical nature. A major task that remains is to apply the elegant mathematical models and methods of analysis that have evolved to actual immobilized kinetic data. Fortunately, guidelines for completing this task have been outlined in both of the references cited above as well as several others

[3133].

Due to the heterogeneous nature of bound enzymes, the catalytic reaction itself is only one in a sequence of important steps that results in the overall transformation of substrate to product. First, the substrate, as well

as ions, inhibitors, and cofactors, must diffuse through the stagnant fluid layer surrounding the solid carrier (external diffusion). Once at the surface, affinity or repulsive effects of a chemical or electrostatic nature may cause a partitioning of these species. This step is followed by reaction with surface-bound enzyme or simultaneous diffusion (internal) and reaction within the carrier and stagnant fluid layer to the bulk solution surrounding the catalyst. With these steps in mind, a number of factors have been identified as affecting the observed or apparent kinetics of bound enzymes; i.e., factors which may cause the bound enzyme to behave much differently than its soluble counterpart. These factors can usually be grouped under two general headings: (1) effects of immobilization on the enzyme molecule itself, and (2) effects on the microenvironment of the bound enzyme. Under the former heading we can consider such factors as conformational changes, matrix interactions, and steric effects which may affect not only the rate of reaction but also the enzyme's catalytic mechanism, specificity, and stability. The second group of factors, often called "microenvironmental effects," includes electrostatic and chemical partitioning effects and external and internal diffusional resistances which result in differences between the macro- and microenvironmental concentrations of substrates, products, or other effectors.

The effects of immobilization on the enzyme molecule itself are not well understood and few experimental studies have been conducted in this area. One major limitation has been the requirement for sophisticated experimental techniques which often must be specially modified for application to immobilized systems. Partitioning effects have frequently been documented in the literature. These effects often manifest themselves in altered pH-activity optima with charged supports and in altered kinetic constants for charged or hydrophobic carriers. Positively charged carriers repel hydrogen ions, resulting in a microenvironmental pH that is higher than the pH of the bulk solution and a shift in pH-activity optima to more acidic pH values. Polyanionic carriers have the opposite effect. By the same mechanism, charged carriers can cause increases in apparent K_m values for substrates carrying like charges and decreases in apparent K_m 's for oppositely charged substrates. Displacements of pH-activity optima of from 12.5 pH units and alterations in K_m 's of more than one order of magnitude have been attributed to electrostatic effects. However, high levels of ionic strength tend to neutralize these effects.

So far the greatest attention has been given to the interaction of enzymatic reaction and diffusional resistances. It has been shown that mass transfer limitations can cause alterations in the apparent temperature dependence of the bound enzyme; in the apparent variation of reaction rate with substrate, product, buffer, and inhibitor concentrations; and even in the apparent operational stability of the enzyme. All of these effects are reversed at high substrate concentrations. It is obvious that in interpreting kinetic data for design purposes it is extremely important to uncouple mass transfer effects from reaction effects, since these two phenomena are affected differently by environmental conditions.

Process Engineering Aspects

Reactor Types

Different types of reactors can be used for process scale operations with enzymes in their free or immobilized forms. The use of free enzymes is often restricted to a batch, stirred tank operation. Continuous processing with free enzymes can be accomplished by employing an ultrafiltration membrane in the process loop. Ideally, the ultrafiltration membrane allows the passage of product and unreacted substrate while retaining the high molecular weight enzyme. The feasibility of using an ultrafiltration membrane reactor has been demonstrated in a few instances.

Continuous flow stirred-tank reactors (CSTR's) have been employed for processing with particulate immobilized enzymes in several cases. These reactors require a means of retaining the bound enzyme in the reaction vessel. This is readily achieved by providing an outlet filter in the reactor by means of a separate settling stage or by the use of an ultrafiltration membrane. Plug-flow reactors (PFR's) are perhaps the most widely used reactor type. Under ideal plug-flow conditions, packed-bed reactors have much higher conversion efficiency than continuous stirred-tank reactors for the same reactor residence time. The use of tubular reactors with porous sheets and porous blocks has also been examined. We have recently developed very efficient tubular reactor configurations in which collagen-enzyme membranes are wound to form spiral multipore modules [32, 34].

Recycle reactors may find their applications when an insoluble substrate is to be processed. Recycle reactor systems for starch hydrolysis and for the treatment of body fluids have been investigated. They are also excellent tools for kinetic studies of immobilized enzymes. The possibility of using fluidized-bed reactors for immobilized enzyme and cell applications has been extensively explored.

The choice of a particular type of reactor would depend on a number of factors as listed in Table 5. Since plug-flow reactors have an innate kinetic

TABLE 5 Factors Affecting the Choice of Reactor Type
1. Form of the immobilized enzyme
particulate, membranous, fibrous
2. Nature of the substrate
soluble, particulate, colloidal
3. Carrier loading capacity
4. Surface-to-volume ratio
5. Mass transfer characteristics
microdiffusional and macrodiffusional efficiencies
6. Throughput capacity of the reactor
7. Reaction kinetics
8. Catalyst replacement, regeneration
9. Ease of fabrication
10. Reactor costs

advantage over the continuous stirred-tank reactors, they may be expected to dominate immobilized enzyme applications. Hydraulic considerations are of paramount importance in their operation.

Columns packed with relatively deformable beads, chips, pellets, or micro-capsules suffer from the inability to achieve sufficient flow rates for industrial scale operation. Increasing the pressure differential across the packed bed in an attempt to augment flow rates is often fruitless because of the compaction and lower hydraulic permeability of the resulting bed. These effects are compounded by the concomitant channeling and dispersion of the substrate, decreasing process yields. However, highly efficient reactor configurations which minimize these disadvantages can be constructed when the carrier is mechanically strong and properly arranged.

Idealized Reactor Design Equations

The important design variables that govern the performance of an immobilized enzyme reactor are (1) reactor space time, (2) substrate feed concentration, (3) the amount of immobilized enzyme used, and (4) the temperature and pH of the reaction. The performance of a reactor can be judged from the fractional conversion X defined as

$$X = \frac{S_0 - S}{S_0} \quad (4)$$

where S_0 and S are the inlet and outlet concentrations of the substrate.

Assuming perfect mixing in a continuous flow stirred-tank reactor (CSTR), and further that the difference in the kinetic behavior of the free and immobilized enzyme can be represented by apparent kinetic parameters, a simple steady-state reactor design equation may be obtained. If the reaction kinetics follow a Michaelis-Menten rate expression, then the performance of the CSTR is given by the following equation (at steady state):

$$X[S_0 + K_m' (1 - X)] = k_2 E_0 \tau \quad (5)$$

where K_m' = apparent Michaelis-Menten constant, k_2 = rate constant, E_0 = enzyme concentration in the reactor, τ = space time in the reactor = V_R/Q , V_R = volume of the reactor, and Q = volumetric flow rate.

Similarly, for an ideal plug-flow reactor, a steady-state reactor design equation can be obtained as

$$S_0 X - K_m' \ln(1 - X) = k_2 E_0 \epsilon \tau \quad (6)$$

where ϵ is the void volume of the reactor bed. The equation for a batch reactor is essentially the same as Eq. (6).

When the inlet substrate concentration is much higher than K_m' , the reaction rate

becomes zero order with respect to substrate concentration

and Eqs. (5) and (6) become identical. In this case the required volume of the reactor or the amount of enzyme required for a given space time is the same irrespective of the reactor type.

When $S_0 \ll K_m'$, the reaction becomes first order with respect to substrate concentrations. The ratio of the amounts of immobilized enzyme required in a CSTR and a plug-flow reactor under these conditions is given by

$$\frac{E_{\text{CSTR}}}{E_{\text{PFR}}} = - \frac{X}{(1-X) \ln(1-X)} \quad (7)$$

It is clear from (7) that the higher the required conversion level, the greater is the relative amount of enzyme required in the CSTR. For example, for 90 and 99% conversion of substrate, approximately 4 and 22 times the amount of enzyme is needed in a CSTR compared to a PFR at a given reactor space time. When S_0 is in the range of K_m' , then the differences in the performance of a CSTR and a PFR would lie somewhere in between these two extreme cases.

The above equations do not include the decay of enzyme activity with time in continuous operation. For most practical purposes, the rate of loss of enzymatic activity under isothermal reactor operation can be represented by a pseudo-first-order process:

$$-dE_0/dt = k_d E_0 \quad (8)$$

where E_0 = effective enzyme concentration in the reactor, k_d = first-order enzyme decay constant, and t = reactor operating time.

Equation (8) can be combined with Eq. (5) and (6) to obtain expressions to describe catalyst decay in a CSTR and a PFR, respectively.

As mentioned earlier, another useful process parameter is reactor productivity, which is the total amount of product produced per unit amount of catalyst in its entire useful life (typically this ranges from two to three half-lives in industrial operation). It is defined by

$$P = \int_0^t A dt \quad (9)$$

where A = instantaneous activity of the catalyst expressed as kilograms of product/kilograms of catalyst/hour, and t = reactor operating time in hours.

Mass Transfer Kinetic Models for Enzyme Reactor Systems

Data obtained from several laboratory reactors have clearly established the presence of mass transfer resistances to transfer of substrate adjacent to and within the immobilized enzyme system. As mentioned earlier, for

the efficient design of an immobilized enzyme reactor, it is essential to develop detailed models that account quantitatively for diffusional effects.

The chemical engineering literature abounds with correlations for predicting fluid phase (external) mass transfer in heterogeneous catalysis. Many of these correlations are applicable to immobilized enzyme/whole cell reactor systems as well. Many of the relevant correlations have been summarized in a recent review [32].

Intraparticle or internal diffusional impedances also influence the kinetics of immobilized enzyme reactions. The enzyme is usually distributed within a porous carrier matrix, and substrate has to diffuse through the carrier to reach the reaction site. In many cases, internal diffusional resistance substantially reduces the expressed catalytic activity of the enzyme.

If we consider an enzyme membrane of nearly infinite expanse and of thickness $2L$, the steady-state balance on substrate diffusing and reacting in the membrane is

$$D_e \frac{d^2 S}{dx^2} - \frac{V_m S}{K_m + S} = 0 \quad (10)$$

which can be solved for a few limiting cases. When $S \gg K_m$, then the reaction becomes first order in S ,

$$V = kS \quad (11)$$

where k = first-order reaction rate constant.

Analytical solution of Eq. (10) for first-order kinetics with appropriate boundary conditions leads to (12), which describes the local substrate concentration as

$$S = S_0 \frac{\cosh \phi \left(1 - \frac{X}{L}\right)}{\cosh \phi} \quad (12)$$

where ϕ = Thiele modulus = $L[k/D_e]^{0.5}$.

An effectiveness factor, η , defined as the ratio of actual reaction rate in the matrix to the (maximum) rate obtainable without diffusional influences, is given by

$$\eta = \frac{\tanh \phi}{\phi} \quad (13)$$

The effectiveness factor η increases with decreasing values of the modulus ϕ (i.e., the diffusion rate is higher with respect to the reaction rate). An effectiveness factor of unity signifies no diffusional limitation. The effectiveness factor is an important design parameter because it measures the extent of internal diffusional resistance.

Effectiveness factors for the general Michaelis-Menten kinetics have been developed by Moo-Young and Kobayashi [35] in terms of a general modulus m defined as

$$m = \frac{LV(S_i)}{\sqrt{2}} \left[\int_0^{S_i} D_e V(S) dS \right]^{0.5} \quad (14)$$

where S_i = substrate concentration at the surface, S = substrate concentration anywhere in the membrane, and $V(S)$ = reaction rate as a function of S .

The pore diffusional effects can thus be quantified through the effectiveness factor, η . The actual reaction rate is obtained by the product of the true chemical reaction rate (in the absence of internal pore diffusion) and the effectiveness factor. For a given reaction system the effectiveness factor depends inversely on the particle size. It is estimated that to obtain a relatively diffusion-free catalyst for the immobilized porous glass-glucose oxidase system, extremely fine particles of 30 μm or less in diameter must be used [8]. These particle sizes would present severe pressure drop problems in an industrial packed-bed reactor. The problem is even more aggravated when substrates of lower diffusivities are to be processed. For example, a commercial reactor using particles of 500 μm diameter for converting a protein substrate having a diffusivity of $4 \times 10^{-7} \text{ cm}^2/\text{s}$ would utilize only about 3% of the available catalytic capacity [8]. Therefore, suitable means must be devised to alleviate the microdiffusional problems.

In many cases, both the external and the internal diffusion effects may be significant, which complicates the reactor design problem even further. Detailed mass transfer-kinetic models describing the steady state and unsteady behavior of a packed-bed reactor under these conditions with nonlinear Michaelis-Menten kinetics have recently been formulated [32]. These models also incorporate the effects of enzyme inactivation and elution from the support matrix.

The problem of transport resistances in the overall reaction assumes even greater importance in the case of immobilized microbial cells. The cell wall and cell membrane present additional transport barriers. In the case of monoenzyme reactions, it is often possible to increase the permeability of the cell by specific treatments. One example in this connection is heat treatment of cells prior to immobilization in the case of cells containing glucose isomerase activity. When concerned with more complex reaction sequences and reaction pathways, this may not be feasible. The total cell structure needs to be retained intact in order to preserve the optimal location of enzymes and cofactor regenerating machinery. It is also worth noting that transport into the cell may not be just passive diffusion.

From the foregoing discussion it is clear that the overall performance of an enzyme reactor would be influenced not only by the characteristics of the immobilized catalyst but also by the manner in which it is packed in a reactor and the reactor operation.

Industrial Applications of Immobilized Enzyme and Whole Cell Systems

The list of potential applications of immobilized enzymes in industry is indeed impressive, although only a handful have actually been commercialized. The largest volume industrial application of immobilized enzymes is in the production of high fructose corn syrup (HFCS). This application involves the isomerization of glucose to fructosea sweeter sugarby immobilized glucose isomerase. The surge in sucrose prices worldwide in 1974 and 1975 was a major impetus in the commercialization of this process. Several billion pounds of HFCS (dry basis, containing approximately 42% fructose) were produced in the United States alone in 1981, and the present installed capacity is estimated to be around 5.5 billion pounds. Small HFCS plants also exist in Holland, Belgium, Italy, Spain, Korea, and Japan. A few additional HFCS plants are also under construction in North America. Some details of the immobilization procedures and the commercial isomerization process are available in the literature [3743].

Several immobilized enzyme or whole cell processes are being practiced commercially in Japan in the pharmaceutical industry. The current applications include the production of (1) L-amino acids from acyl-D, L-amino acids, (2) L-aspartic acid from ammonium fumarate, (3) L-citrulline from L-arginine, (4) urocanic acid from L-histidine, (5) L-malic acid from fumaric acid, and (6) 6-aminopenicillanic acid. Immobilized whole cells are employed in applications (2) through (6).

Use of immobilized penicillin acylase in the hydrolysis of penicillins to generate the semisynthetic penicillin intermediate 6-aminopenicillanic acid is also a commercial reality in the United States and Europe. Whole milk lactose hydrolysis by fiber entrapped lactase is reportedly being carried out on a relatively moderate scale in Italy.

Many other applications of immobilized enzymes and cells have reached the point at which serious consideration for commercialization is warranted. Included in this group are (1) saccharification of starch by immobilized gluco-amylase; (2) cheese whey lactose hydrolysis by bound β -galactosidase; (3) beer chill proofing; (4) steroid transformations; (5) protein hydrolysis to improve solubility, taste, and digestibility; (6) removal of residual oxygen in various food products; (7) milk coagulation for cheese making; (8) production of ethanol; and (9) production of L-lysine from DL-amino caprolactam. Other possible applications include large-scale preparation of galacturonic acid, structure modification of cephalosporin C, synthesis of L-tryptophan from indole and serine, starch conversion of maltose, production of drug metabolites, and synthesis of gramicidin.

In summary, it may be stated that spurred by the phenomenal success of immobilized glucose isomerase in the production of HFCS, the industry is actively pursuing various other applications of bound enzyme systems. Many new processes are likely to be commercialized in the years ahead.

There are also a number of applications in the analytical (laboratory) and medical fields which have been summarized in several excellent reviews [44].

Commercial Enzyme Reactor Systems: Design Considerations and Operational Strategies

Commercial Catalyst Systems

As stated earlier, enzymatic isomerization of dextrose to fructose represents the largest commercial use of immobilized enzyme technology to-date. Since there are several plant scale operations in place, it is useful to employ this as a model system to discuss the bases for commercial enzyme reactor design and operation. A flow sheet for the commercial production of HFCS is shown in Fig. 2.

Immobilized glucose isomerase is available commercially from a number of suppliers. From a user's point of view, an objective comparison of the performance of different catalysts is essential. However, enzyme suppliers' data are often provided on different bases. A ready comparative evaluation of competing systems is, therefore, quite difficult. The user's laboratory and pilot plant have to be employed to develop performance data on a unified basis. Such data can then be used to choose the optimum catalyst system.

Several processing parameters to be evaluated in this connection are

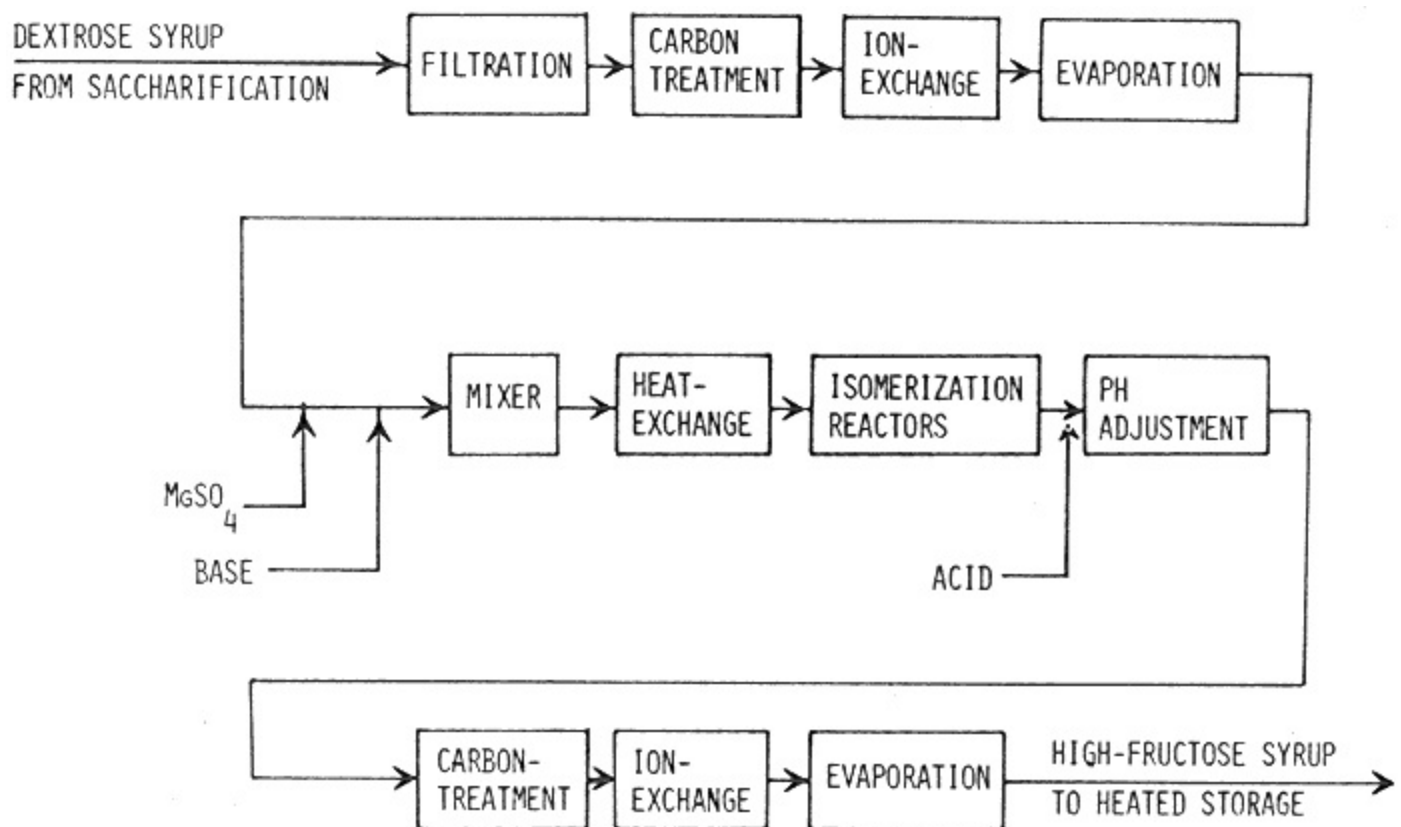


Fig. 2.
Flow sheet for the production of high fructose corn syrup (HFCS).

TABLE 6 Glucose Isomerization: Reactor Design Parameters

I. Biochemical characteristics:

1. Activity
2. Operational stability (half-life) and activity decay profile
3. Productivity in usage lifetime
4. Optimal substrate concentration
5. Effect of oligosaccharides concentration
6. Effect of dissolved oxygen
7. Minimum and maximum residence times
8. By-product formation
9. pH and temperature sensitivity
10. Storage stability
11. Protein-enzyme elution
12. Microbial growth, if any
13. Reactor effluent quality (composition, color, odor, protein content, pH, etc.)

II. Mechanical characteristics:

1. Particle size, shape, and size distribution
2. Density (dry bulk density and wet density)
3. Swelling behavior
4. Compressibility
5. Cohesion
6. Particle attrition

III. Hydraulic characteristics:

1. Pressure drop
2. Mode of flow (upflow versus downflow)
3. Bed compaction
4. Axial dispersion and channeling
5. Residence time distribution
6. Stratification
7. Length-to-diameter ratio
8. Minimum velocity for onset of fluidization

summarized in Table 6. They are grouped under three different categories: biochemical, mechanical, and hydraulic characteristics.

The physical properties of a commercial immobilized enzyme are tabulated in Table 7. Most of the parameters are self-explanatory. The

TABLE 7 Immobilized Glucose Isomerase Physical Properties
(product of ICI)

Product form:	Dry pellets
Mesh size:	Nominally 12 × 20 mesh
Dry bulk density:	4045 lb/ft ³
Wet bulk density:	14 lb/ft ³ + 10%
Active assay:	40 mμ/g, a minimum
Productivity:	Normally 2000 lb, 42% dry basis HFCS/lb catalyst in 1000 h

Bed void Estimated at 45%

aOne unit is defined as the amount of catalyst that would convert
10⁻⁹ mol of substrate per minute at 60°C, pH 8.0.

critical one is the overall productivity of the catalyst. It has a typical value of 2000 lb of 42% fructose syrup per pound catalyst in 1000 h of operation. Given proper feed and operation, typical half-life values are in the range of 400 to 500 h. Taken altogether, these two factors dictate the overall reactor size required to accomplish the desired throughput and conversion level. From an effective evaluation on the lines of the factors indicated in Table 6 combined with the catalyst cost the optimum enzyme system is chosen for use in commercial production facility.

Design Strategies

Since the activity of the bound enzyme decreases continuously, it is necessary to have a number of reactor columns in contrast to one gigantic column. This would minimize production fluctuations with respect to capacity and conversion level. For a given plant capacity, the optimum number of columns can be estimated theoretically. Most commercial plants have at least six columns in the reactor battery.

Both series and parallel operation of the reactor system are possible. In series operation there are fewer streams to control, and the upstream bed in a series can be nearly fully exhausted before removing it from service. However, the latter point is not of great relevance since exhaustion of bed activity is very gradual. Furthermore, series operation suffers from one overriding disadvantage: fluid velocity. For the same throughput a three-column series will have triple the velocity as the same system with three columns in parallel. Therefore, the potential for pressure drop and compaction problems are greatly enhanced. Parallel operation, on the other hand, offers the greatest operational flexibility. Each reactor can be operated essentially independent of others. Each column can be brought into and taken out of service very readily.

Another consideration relates to upflow versus downflow operational mode. Upflow operation offers the advantages of good fluid/particle contact and constant minimum pressure drop. The downflow mode allows operation under essentially atmospheric pressure where the fluid flow through the bed is controlled readily by the hydraulic head above the bed. Therefore, the preferred reactor design appears to be a number of fixed bed columns operating in the parallel mode in which fluid flow occurs in the downflow fashion.

Column Hydraulics

The hydraulic considerations dictate the maximum permissible bed depth. The swollen enzyme particles form a compressible bed. Under normal downflow operating mode, compression is insignificant and the behavior of the beds is close to that of the rigid granule. On the other hand, under severe hydraulic force the bed will compact and pressure drop will increase with time. The hydraulic force is greatest in the freshly formed bed when activity (hence throughput) is highest.

Reactor Kinetic Analysis

The overall isomerization reaction of dextrose to fructose is characterized by the sequence of steps involving mass transport, biochemical complex formation, and biochemical reaction. Detailed mass transfer-kinetic models have been developed. However, under practical operating conditions it is possible to simplify the kinetic expression to the following form:

$$\tau = \frac{X_e S_0}{V_m} \left[\frac{K_m}{S_0} + 1 \right] \ln \left[\frac{X_e - X_i}{X_e - X} \right] \quad (15)$$

where τ = effective reactor residence time

S_0 = feed concentration

V_m, K_m = constants

X_e = equilibrium conversion

X_i = initial conversion

X = conversion at reactor exit

The above equation is an integrated flow of the plug-form reactor equation predicting a first-order dependence of the reaction rate on dextrose concentration.

Figure 3 shows a typical catalyst decay profile over the entire operational life of the catalyst. This decay rate can also be described quantitatively as a first-order process and can be characterized conveniently in terms of a catalyst half-life (the time required for the activity to decrease by 50%). Using the reactor kinetic model along with the catalyst decay profile, it is possible to predict the performance of the catalyst over a long operating period. A detailed computer program based on such a model can be used as an on-line process control tool.

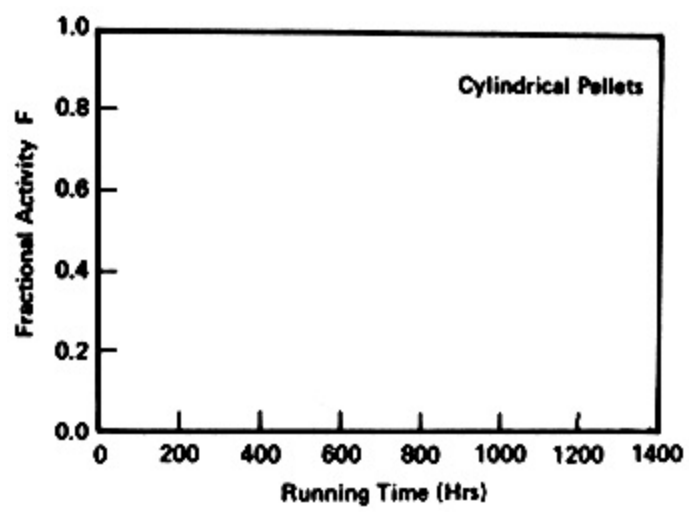


Fig. 3.
Enzyme activity decay profile.

Operational Considerations and Process Control Strategies

Adequate provisions must be made to complete swelling (rehydration) of the dry immobilized enzyme particles prior to regular column operation. This is facilitated by preswelling the particles in a separate vessel and then transferring them to the reactor column. Uniformity of bed packing is also mandatory to achieve good flow distribution.

In downflow operation the substrate percolates through the packed bed by gravity; to accomplish this, a sufficient liquid head above the bed must be maintained at all times. Feed inlet and outlet should also be so designed to insure that the packed bed is never allowed to become dry. Start-up and shut-down procedures must be developed to obtain maximum efficiency of the enzyme as well as ease of column switchover.

It is necessary to operate the reactor system to obtain a finished product of uniform quality and constant fructose content (typically 42% dry solid basis). On-line measurements of fructose and glucose levels and a priori knowledge of the catalyst decay profile are employed as feedback mechanisms to control the flow rate through the reactors. In practice, flow cannot be precisely controlled at all times to get 42% fructose in the product, but it can be achieved on an averaged basis.

The effect of temperature on overall productivity can be dramatic. A feed temperature of 60°C is considered optimum. Higher temperatures result in faster flow rates but also accelerate enzyme decay and vice versa.

The most critical operating parameter is pH in the bed. Since it is difficult to control pH directly in the column, pH adjustment is limited to precolumn feed conditioning. Ideally, the effluent pH from the column is 7.8 to 8.0 at 60°C. Even small deviations in operating pH have a significant effect on productivity of the column.

Typically, a single reactor column is operated for a period of three half-lives, after which the enzyme is replaced with a fresh batch. Practical flow rate limitation and maximum allowable reactor residence time (mentioned earlier) dictate the cut-off point for a given reactor. Modest variations in operating temperature and conversion level, followed by back-blending, are important process control strategies. Since the conversion level is far less sensitive to flow rate changes above 42%, modest changes in conversion can also be used as an additional process control strategy to optimize the reactor battery's performance. It is possible to control the entire operation on-line through a minicomputer or microprocessor.

Process Economics

The foregoing sections illustrate how different competing considerations come into play in terms of the overall plant design for HFCS. These factors affect not only the initial capital outlay but also the operating costs. Depending upon the location and capacity level, the capital cost of a high fructose syrup plant would vary between 8 and 12 cents per pound

of HFCS (dry basis) per year. Isomerization enzyme cost is a significant

fraction of the overall cost. Generally speaking, the isomerization cost works out to be between 50 and 60 cents per hundred weight HFCS dry basis. At current selling prices for HFCS, the overall process economics is improved by every percent increase in enzyme productivity.

Symbols

A	catalytic activity of immobilized enzyme
ADP	adenosine diphosphate
ATP	adenosine triphosphate
AMP	adenosine monophosphate
D_e	effective diffusivity
d_p	diameter of catalyst particle
E_0	enzyme concentration in the reactor
K_m, K_m	Michaelis-Menten constant for free and immobilized enzymes, respectively
K_p	(competitive) product inhibition constant
K'_p	noncompetitive product inhibition constant
K_d	enzyme decay constant
K_L	mass transfer coefficient
k, k_1, k_{-1}, k_2	reaction rate constants
L	half thickness of enzyme-membrane
m	generalized Thiele modulus
NAD	nicotinamide adenine dinucleotide
NADP	nicotinamide adenine dinucleotide phosphate
P	product concentration
P	reactor productivity
Q	flow rate through reactor
S	substrate concentration
V	reaction rate

V_m	maximum reaction rate
X	fractional conversion

Greek Letters

ϕ	Thiele modulus
η	effectiveness factor
ρ	activity yield
τ	reactor residence time

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Esterification

Robert M. Simons

This article deals with the production of carboxylic estersorganic compounds with the structure $\text{R}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}-\text{R}$. Carboxylic esters are usually produced by the reaction of an alcohol and a carboxylic acid to form the

ester and water. The reactions is generally characterized by high yield with few side reactions. Other methods for ester formation utilize carboxylic acid derivatives such as acid anhydrides, acid chlorides, nitriles, and amides. Esters can also be produced from unsaturated hydrocarbons and aldehydes. This article will be concerned with ester production by the reaction of an alcohol and carboxylic acid or anhydride. Reviews on the subject of esterification are given in Refs. 14.

Commercial Significance

From a volume standpoint, esterification represents one of the most important reactions of the chemical industry. The number of different esters produced for commerce by over 100 manufacturers probably exceeds 500. These materials cover a broad range of uses and include plasticizers, flavors and fragrances, pesticides, solvents, medicinals, surface-active agents, chemical intermediates, and monomers for resins and high molecular weight polymers. Table 1 lists 1979 production in the United States for several end-use categories [5].

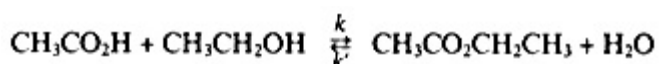
TABLE 1 1979 U.S. Production, Sales Volume, and Value of Selected Esters [5]

	Production, Million lb	Sales	
		Million lb	Million \$
Plasticizers:			
Phthalates	1290	1232	455
Adipates	75	64	35
Trimellitates	20	18	10
Solvents:			
Ethyl acetate	262	156	29
n-Butyl acetate	139	119	35
Propyl acetate	51	51	15
Monomers:			
Ethyl acrylate	316	148	50
Butyl acrylate	297	157	60
2-Ethylhexyl acrylate	68	58	26
Surface-active agents:			
Carboxylic esters	254	196	133
Pesticides:			
Octyl-2,4-dichlorophenoxyacetate	8	9	7

Principles of Esterification of a Carboxylic Acid with an Alcohol

Equilibrium

The acid catalyzed reaction of a carboxylic acid and an alcohol to form an ester and water is a reversible process. Early studies [6] showed that when equal molar proportions of acetic acid and ethanol were heated until no further increase in product was found, about 67 mol% of each of the starting reactants had been converted to ester. Conversely, when equal molar quantities of ethyl acetate and water were heated together, approximately 33% of the ester was converted to acetic acid and ethanol. Conversions of over 67% were obtained by increasing the mole ratio of alcohol to acid. In the reaction of acetic acid and ethanol,



the rate of esterification can be represented by $k[\text{CH}_3\text{CO}_2\text{H}][\text{CH}_3\text{CH}_2\text{OH}]$, where the quantities within the brackets represent the molar concentration of the reacting species, and the rate of hydrolysis by $k'[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]$. Thus, if the concentrations are those at equilibrium, then

$$k[\text{CH}_3\text{CO}_2\text{H}][\text{CH}_3\text{CH}_2\text{OH}] = k'[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]$$

and

$$\frac{k}{k'} = K = \frac{[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}][\text{CH}_3\text{CH}_2\text{OH}]}$$

The constant K is called the equilibrium constant of the reaction. Different concentrations of reactants and products can be present initially, but when equilibrium is obtained the concentrations of the different species will be related such that the equilibrium expression holds. This statement needs some qualification as different workers have reported variations in the equilibrium constant with large changes in the concentration of the reactants or products, acid catalyst concentration, or changes in solvent [7]. Even though molar concentrations are usually used instead of activities, K remains fairly constant as long as the overall system is not dramatically changed.

The value of K will depend on the particular carboxylic acid and alcohol and is determined experimentally by allowing the reaction mixture to reach equilibrium and analyzing for reactants and products. Table 2 shows the effect of reactant ratio on conversion to ester for different values of K .

In general, the numerical value of the esterification constant varies

TABLE 2 Effect of Reactant Ratio on Theoretical Conversion to Ester for Different Values of K

Equilibrium Constant, K	Mole Ratio of Reactants	Theoretical Conversion (%) to Ester at Equilibrium
0.1	1	24.0
0.1	5	48.3
0.1	10	60.7
1	1	50.0
1	5	83.3
1	10	90.0
3	1	63.4
3	5	92.9
3	10	96.6
5	1	69.1
5	5	95.5
5	10	97.9
10	1	76.0
10	5	97.6
10	10	98.9

between 1 and 10 for various primary and secondary alcohols and carboxylic acids. The primary alcohols have a higher value than secondary alcohols. Tertiary alcohols are generally much less than unity, and direct esterification with a carboxylic acid is not practical since dehydration of the alcohol will generally occur much more readily than esterification. Table 3 lists some equilibrium constants for different alcohols with acetic acid and for different acids with isobutanol compiled from extensive early work of Menshutkin [8].

The heat of reaction for many esterifications is near zero or at least quite small. For these reactions the equilibrium constant is essentially independent of temperature.

TABLE 3 Equilibrium Constants for Esterification of Acetic Acid with Different Alcohols and for Isobutanol with Various Acids [8]

Acetic Acid + Alcohol	K	Isobutanol + Acid	K
Methanol	5.2	Formic	3.2
Ethanol	4.0	Acetic	4.3
Propanol	4.1	Propionic	4.8
Butanol	4.2	Butyric	5.2
Isopropanol	2.4	2-Methylbutyric	7.9
2-Butanol	2.1	Pivalic	7.1
3-Pentanol	2.0	2,2-Dimethylbutyric	8.2
t-Butanol	0.005	p-Toluic	7.0

Effect of Structure

Although the equilibrium constant indicates the extent to which the esterification reaction will proceed, it tells nothing about the rates of reaction. The rate of esterification is affected much more dramatically than the position of equilibrium by changes in the structure of the reactants. The largest change is due to steric effects with relatively little influence due to polar effects. For example, Table 4 gives the relative rates for the acid-catalyzed esterification of substituted benzoic acids in methanol [9].

The kinetic effect of substituting bromine or a nitro group for methyl in the para position of the aromatic ring is relatively small. Substitution of a group in the ortho position produces a marked retarding influence when the rate is compared with the same groups in a para or meta position. Substitution of two groups in the ortho positions essentially prevents esterification under ordinary conditions [10]. In the aliphatic series, chain branching near the reactive site has a very large effect on the reaction rate. Table 5 shows this influence for various aliphatic acids [11].

Reaction Mechanism

Since the acid catalyzed esterification of a carboxylic acid with an alcohol is experimentally reversible, the reverse reaction acid hydrolysis of esters will have the same mechanism in its respective direction. Thus, if the mechanism for acid hydrolysis is determined, the mechanism for the acid-catalyzed esterification is also established.

Most common acid-catalyzed esterification and hydrolysis reactions occur by cleavage between oxygen and the acyl group:

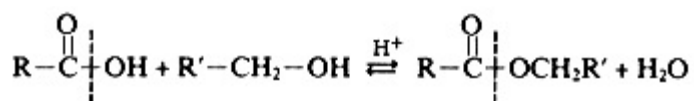


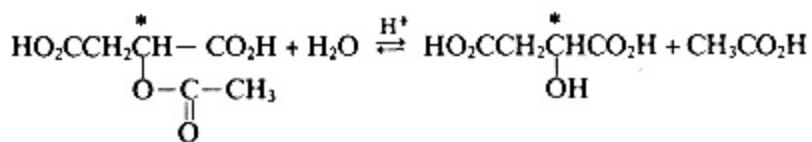
TABLE 4 Relative Reaction Rates for the Acid Catalyzed Esterification of Aromatic Acids with Methanol at 40°C [9]

Acid	Relative Rate
C ₆ H ₅ CO ₂ H	1
p-CH ₃ C ₆ H ₄ CO ₂ H	0.91
m-CH ₃ C ₆ H ₄ CO ₂ H	1.0
o-CH ₃ C ₆ H ₄ CO ₂ H	0.31
p-BrC ₆ H ₄ CO ₂ H	0.61
m-BrC ₆ H ₄ CO ₂ H	0.62
o-BrC ₆ H ₄ CO ₂ H	0.29
p-NO ₂ C ₆ H ₄ CO ₂ H	0.42
m-NO ₂ C ₆ H ₄ CO ₂ H	0.36
o-NO ₂ C ₆ H ₄ CO ₂ H	0.04

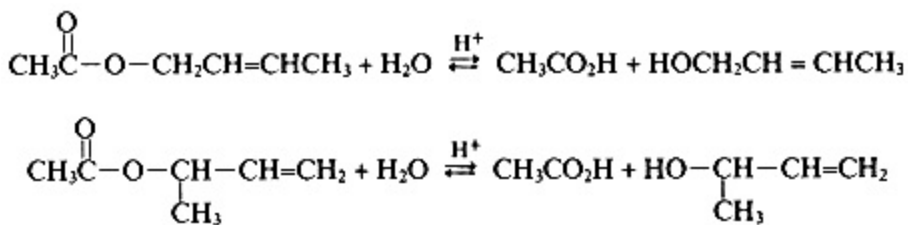
TABLE 5 Relative Rates of Acid Catalyzed Esterification of Aliphatic Acids with Methanol at 40°C [11]

Acid	Relative Rate
CH ₃ CO ₂ H	1.0
CH ₃ CH ₂ CO ₂ H	0.84
CH ₃ CH ₂ CH ₂ CO ₂ H	0.49
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCO}_2\text{H} \end{array}$	0.33
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CO}_2\text{H} \\ \\ \text{CH}_3 \end{array}$	0.04
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CO}_2\text{H} \\ \\ \text{CH}_3 \end{array}$	0.02
$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{CH}-\text{CH}_2\text{CO}_2\text{H} \\ \\ \text{CH}_3 \end{array}$	0.0006
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5-\text{C}-\text{CO}_2\text{H} \\ \\ \text{C}_2\text{H}_5 \end{array}$	0.0002

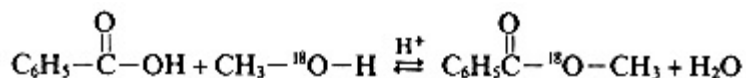
A considerable amount of evidence supports this statement. Holmberg showed that the configuration of the asymmetric carbon in acetoxysuccinic acid is retained on acid hydrolysis [12]:



No isomerization of the alcohols takes place during acid hydrolysis and esterification with crotyl acetate or 1-methylallyl acetate [13]:



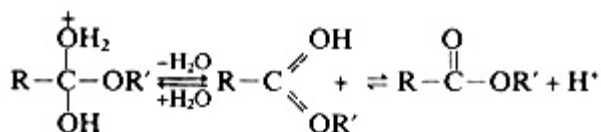
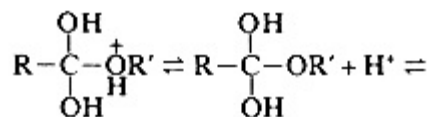
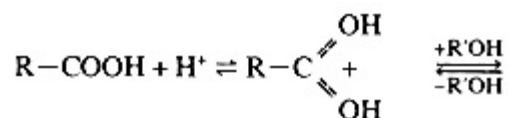
Esterification of benzoic acid and methanol labeled with ^{18}O gave water with the normal isotopic composition [14]:



A study of acid hydrolysis in which ^{18}O labeling has been used to support acyl oxygen cleavage includes the hydrolysis of methyl hydrogen succinate [15], γ -butyrolactone [16], and the trifluoroacetates of methanol [17].

Experiments with the acid hydrolysis of ethyl benzoate labeled in the carbonyl group with ^{18}O indicate that the intermediate has a lifetime long enough to allow appreciable oxygen exchange with the solvent [18].

From the foregoing experimental work and from kinetic considerations, the mechanism for the more common acid-catalyzed esterification and hydrolysis reactions can be written as follows [1]:



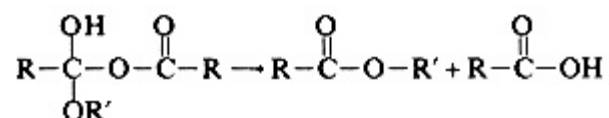
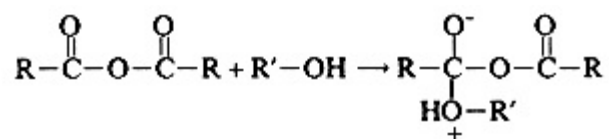
It was noted earlier that structural changes have profound effects on the rate of esterification but make relatively little difference on the position of equilibrium. In examining the bimolecular mechanism for acid-catalyzed esterification and hydrolysis, the reactants and intermediates for the two reactions are very similar and, as expected, the steric effects in ester hydrolysis are nearly the same as for esterification. In addition, the specific rates of esterification and hydrolysis should vary in the same manner with structural changes in the reactants. Thus the equilibrium constantthe ratio of these specific rate constantsshould show little change with structure. In addition, the mechanism points out why smaller polar effects are noted in esterification and hydrolysis reactions. Those polar groups which would facilitate the addition of a proton would retard the attack by alcohol in esterification or water in hydrolysis. However, strong steric effects would be expected since the reaction is bimolecular.

Esterification of a Carboxylic Anhydride with an Alcohol

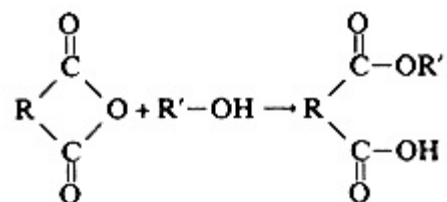
In contrast to carboxylic acids, the reaction of carboxylic anhydrides with alcohols is not a reversible process and can go to completion without removal of the carboxylic acid produced:



Anhydrides are also much more reactive than carboxylic acids. It is usually sufficient to heat a mixture of the anhydride and alcohol to bring about complete reaction. Various workers have determined that the reaction is second order, which is consistent with a bimolecular mechanism analogous to carboxylic acid esterification [19]:



The reaction is catalyzed by acids [20] and bases [21]. General base catalysis is indicated for the rate enhancement by pyridine for acylation of phenols [22]. It has been suggested that acylation with anhydride in the presence of sulfuric acid involves the initial formation of the mixed anhydride of sulfuric acid and the aliphatic acid [23]. Anhydrides of dibasic carboxylic acids react readily with alcohols to form the monoalkyl ester [24]:



Esterification of the carboxylic acid then becomes a matter of esterification of a carboxylic acid with an alcohol and is governed by the principles previously discussed.

Technical Considerations

The esterification of a carboxylic acid with an alcohol is extremely slow at ambient temperatures. As a rule of thumb, the rate of esterification like other organic reactions is approximately doubled by a 10°C rise in temperature. However, in contrast to carboxylic anhydrides, heating the reaction mixture of the carboxylic acid and alcohol to the atmospheric boiling point of the mixture generally still does not provide a practical rate of esterification. Again, in contrast to the carboxylic anhydrides, the extent of the reaction of carboxylic acids will be governed by the equilibrium constant so that complete conversion cannot be obtained. As was pointed out, this is also true for completing esterification of the monoesters from anhydrides of dibasic carboxylic acids.

Thus for practical applications the major concern is for increasing the reaction rate and for establishing conditions which will allow high conversions to be obtained.

Esterification Catalysts

It has long been known that mineral acids greatly increase the rate of esterifications. The most commonly used mineral acid is probably sulfuric acid. It is effective and not as corrosive to metals as hydrogen chloride. Close control is required since even modest increases in concentration or temperature can cause dehydration of alcohols to ethers or olefins. Problems with formation of color bodies may also be a concern. Concentrations of from a few tenths to 1 or 2% by weight are generally employed.

The sulfonic acids also have good catalytic activity and generally cause fewer side reactions than sulfuric acid. The isomers of toluenesulfonic acid are widely used. A somewhat higher concentration of the sulfonic acid may be required in order to achieve the same reaction rate that can be obtained with a given quantity of sulfuric acid.

Ion-exchange catalyzed esterification reactions utilize ion-exchange resins in place of mineral acids. The resins usually employed are sulfonic acid cation exchangers in the hydrogen form. Since the catalyst is a material which is particulate, separation of the product and catalyst is easily achieved by mechanical means. The use of these materials as catalyst in esterifications include the preparation of butyl oleate [25], monoesters of diethylene glycol [26], methyl benzoate [27], ethyl esters of substituted acetic acids [28], and the vapor-phase esterification of 2-propanol with acetic acid [29]. Yields of 98% were obtained in the acetylation of salicylic acid with acetic anhydride using an ion-exchange resin [30]. A continuous system employing a resin bed was used to prepare isoamyl itaconate [31]. Other examples can be found in the review articles by Polyanskii [32].

While strongly acidic catalysts are still generally used for the manufacture of low to medium boiling esters, metallic catalysts have been developed for higher boiling esters such as dioctyl phthalate. Coenen has shown

TABLE 6 Effect of Catalyst on Reaction Rate in Preparation of Bis(2-ethylhexyl) Phthalate [37]

Catalyst	Reaction Time (h)	Conversion (%)
None	45	99.9
H ₂ SO ₄	2.5	99.9
H ₃ PO ₄	25	99.9
Al ₂ O ₃ aq	7	99.9
Al ₂ O ₃ + NaOH	2.5	99.9
Pb(OH) ₂	4.5	99.9
Sn(OH) ₂	7	99.6
Zn(OH) ₂	5	99.6

that fast reaction rates can be obtained with aluminum oxide and with lead, tin, and zinc hydroxides in the preparation of bis(2-ethylhexyl) phthalate [33]. Table 6 shows comparative esterification times at a 2-ethylhexanol to phthalic anhydride mole ratio of 4 and reaction temperatures of 200–210°C. Water was removed as formed. The acid catalyst concentrations were 0.2% by weight of the phthalic anhydride. It was shown that the effective metal catalyst concentration was that of the metal in solution which for the Al₂O₃-NaOH system was 50 ppm aluminum and 100 ppm sodium.

Lower color products resulted from the use of metal catalysts than with either no catalyst or with acidic catalysts. In addition, the formation of ethers and olefins from the alcohol was eliminated with the metal catalysts so that the alcohol could be recycled directly. Short reaction times and high yields are also claimed for tetraalkyl titanates and zirconates in the preparation of higher boiling esters [34]. Table 7 illustrates the reaction times and conversions for the preparation of bis(2-ethylhexyl) phthalate using these catalysts. The alcohol was used in excess, and water was removed from the refluxing reaction mixture as formed. The catalyst concentration varied from 1.35 to 2.7% of the weight of phthalic anhydride used.

TABLE 7 Reaction Times and Conversions Obtained in Preparation of Bis(2-ethylhexyl) Phthalate with Titanium and Zirconium Catalysts [34]

Catalyst	Reaction Time (h)	Conversion (%)
Tetraisopropyl titanate	1.6	99.7
Tetraphenyl titanate	2.7	99
Hydroxy titanium stearate	2.4	99
Tetrastearyl titanate	4.0	99
Tetraethyl zirconate	3.0	99.2
None	19	99

Nozawa has recently reviewed the area of catalysis in the production of bis(2-ethylhexyl) phthalate [35]. The catalysts used for this product should be effective for other higher boiling esters as long as the temperature range (generally above 180°C) can be obtained.

Completing the Esterification Reaction

Since the esterification of a carboxylic acid with an alcohol is an equilibrium reaction, it is necessary to displace the equilibrium in order to obtain high conversions. This is done by removing one or both of the products. In practice this is almost always achieved by azeotropic distillation. The actual operating conditions will depend on the carboxylic acid and alcohol used. Not only must the boiling points and compositions of the binary and ternary azeotropes be considered, but also the solubilities of the alcohols and esters in water.

In the production of nonvolatile esters for which the alcohol is not appreciably soluble in water the water may be removed as the alcohol-water azeotrope. After condensing the vapors, the water layer is withdrawn from a decanter while the organic layer is returned to the column. The process can be run under pressure or under reduced pressure in order to maintain the desired reaction temperature and reflux of the alcohol. Should the alcohol be nonvolatile or fairly soluble in water, an inert liquid such as toluene can be used to form a binary azeotrope with water. In either case the reaction will proceed since water is removed from the reaction mixture. It will also be necessary to check for binary and ternary azeotropes involving these inert liquids for the particular system.

Many of the volatile esters form binary azeotropes with water and with the alcohols from which they are derived. In addition they may form ternary azeotropes generally the lowest boiling with the alcohol and water. For these systems the ester, water, and alcohol of the approximate ternary concentration distill through an efficient column, are condensed, and the aqueous phase containing some ester and alcohol is removed from the decanter for further separation. The organic phase is returned to the column in a batch operation or removed for further purification in a continuous system. In this case both products of the reaction are removed which allows the esterification reaction to proceed. Separation of the product then becomes a matter of distillation.

Esterification Processes

By employing the principles and considerations of the preceding sections, a large number of industrial esterification processes have been developed. The descriptions that follow will be for processes involving esterification of a carboxylic acid or anhydride with an alcohol. Batch and continuous

processes are covered since both are used in industry, depending on the product volumes. Continuous processes are usually employed for large volume products since less labor is involved and conversion cost is lower. Batch processes are mainly used when a number of different products are made on the same equipment in relatively small volume.

Volatile esters are generally refined by distillation and require no neutralization of acid catalyst. For esters with high boiling points such as plasticizers the trend has been to produce a low color and low acid product by a process which does not require high vacuum distillation. This saves on energy, cost, and capital investment. The general steps for production of such a product are reaction removal of excess alcohol by distillation, neutralization, drying, filtration to remove salts, steam treatment for deodorization, decolorization by activated carbon, and final filtration [33, 36].

Plant size and materials of construction are dependent on volumes and types of products produced. Generally the more common stainless steels are satisfactory, but if strong acids are used as catalysts, a more resistant alloy may be needed. Extensive corrosion testing should be done to determine the best materials of construction.

The following general descriptions are examples which may serve as guides for designing specific esterification processes.

Volatile Esters

Manufacture of many of the low to medium boiling esters uses processes which take advantage of binary or ternary azeotropes to remove the water of reaction. A flow diagram for a batch process for such esters is shown in Fig. 1. The carboxylic acid, alcohol, and catalyst (generally a strong acid at a concentration of 12% of the total charge) are fed from their respective tanks to the reactor or base heater of an efficient distillation column. The column ordinarily will be 30 to 40 ft of packed bed or an equivalent number of trays depending on the product mix manufactured on the equipment. The reaction charge depends on the ester being produced but generally contains an excess of the alcohol since it will be part of a binary and/or ternary azeotrope. In addition, the acid and the dry ester may have close boiling points such that it is desirable to consume the carboxylic acid to avoid later separation by distillation. This is especially important for most commercial solvents as the acid limit may be less than 0.01%. The process is started by applying steam to the reactor heater until reflux commences. After a period of reflux, liquid from the condenser will form a two-phase system in the decanter. The organic phase is returned to the column as reflux while the aqueous layer is removed and fed to the flash column where organics are steam distilled for recycle. The water (containing only parts per million organics) is pumped to waste treatment facilities. The process continues to run in this manner as the top temperature lines out at the temperature of the ester-alcohol-water ternary (or ternary-binary) mixture. The aqueous phase is continually removed. The reaction mixture may be adjusted by feeding more alcohol. As conversion

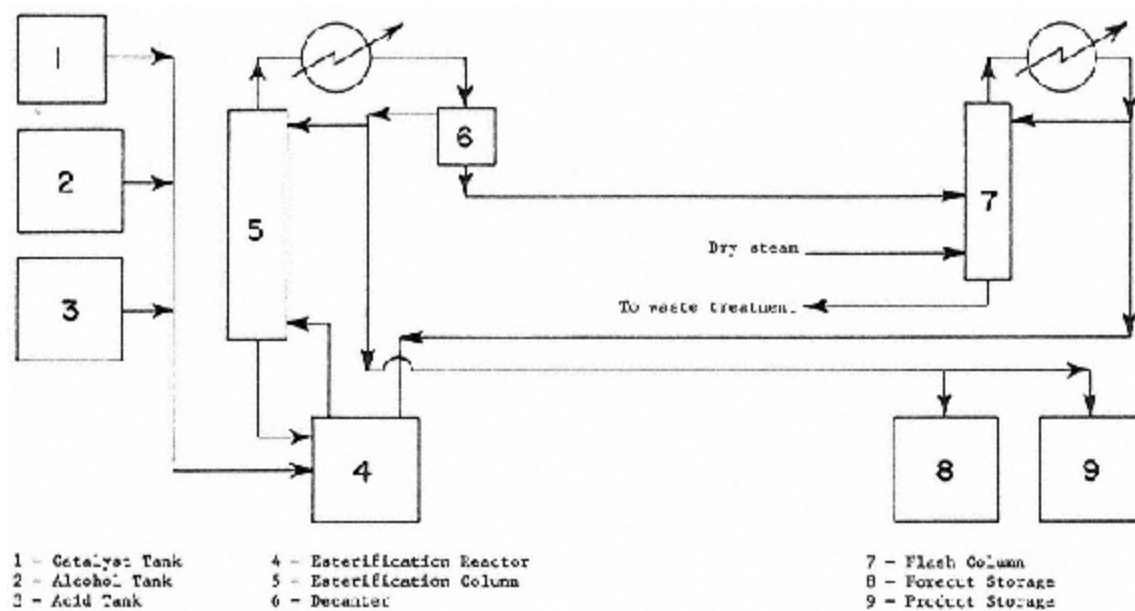


Fig. 1.
Batch esterification: Volatile ester.

to ester becomes complete, water evolution will cease and the temperature readings of the column will show an increase. Takeoff of organic material commences and continues until the top column temperature reaches the boiling point of the ester. The forecut material is stored for use in subsequent runs. The distillate is sampled for product specifications and after quality is confirmed taken off to product receivers. The product is removed at a sufficient reflux ratio to assure adequate fractionation until an established base level is reached. After the reactor is cooled to a temperature below the lowest boiling azeotrope, the forecut material, fresh carboxylic acid, and alcohol are charged. The procedure just described is again followed. These cycles are repeated catalyst concentrations are determined and additional catalyst may be added between batches until the unit is switched to another product or until a buildup of high boilers or carbonaceous materials require a cleanout of the reactor. The organics are then steam distilled and saved for subsequent recycle. The aqueous slurry of high boilers is neutralized and incinerated or sent to wastewater treatment.

A typical continuous process is shown schematically in Fig. 2. Start-up of the continuous unit is very similar to that of the batch process. The alcohol, carboxylic acid, and catalyst are charged to the esterification reactor which is generally smaller than for a batch reactor. The reaction mixture is heated to reflux and after a water phase starts forming in the decanter, acid and alcohol are fed continuously to the esterification reactor. The water layer containing some alcohol and ester is continuously removed from the decanter and fed to the flash column where it is contacted with steam. The alcohol and ester distillate is returned to the reactor and the water, essentially free of all organics, is collected and sent to waste treatment facilities. The ester collects in the organic phase of the decanter along with some alcohol, water, and perhaps traces of acid. A portion of the organic phase is returned to the column as reflux and the remainder is fed to a low boiler column. The low boiler column is of approximately the same size as the esterification column and its purpose is to remove alcohol and water from the crude ester. The alcohol, water, and some ester are removed from the top of the column and returned to the esterification reactor. The dry, alcohol-free ester moves down the column to the base heater and is fed to the refining column base heater. The refining column (1015 trays) is used to assure good color of the product and to free it of any high boiling components. The purified product is collected in tanks and, after quality is confirmed, transferred to storage.

In some esterification processes it may be desirable to use an inert azeotroping agent for water removal. This may be the case for processing relatively high boiling alcohols. The batch process would be operated in much the same manner as previously described with the exception that water removal is achieved with the added agent. If the carboxylic acid is more volatile than the product, an excess of the acid can be used to complete conversion of the alcohol. The excess acid can then be removed by distillation when reaction is complete followed by distillation of the product.

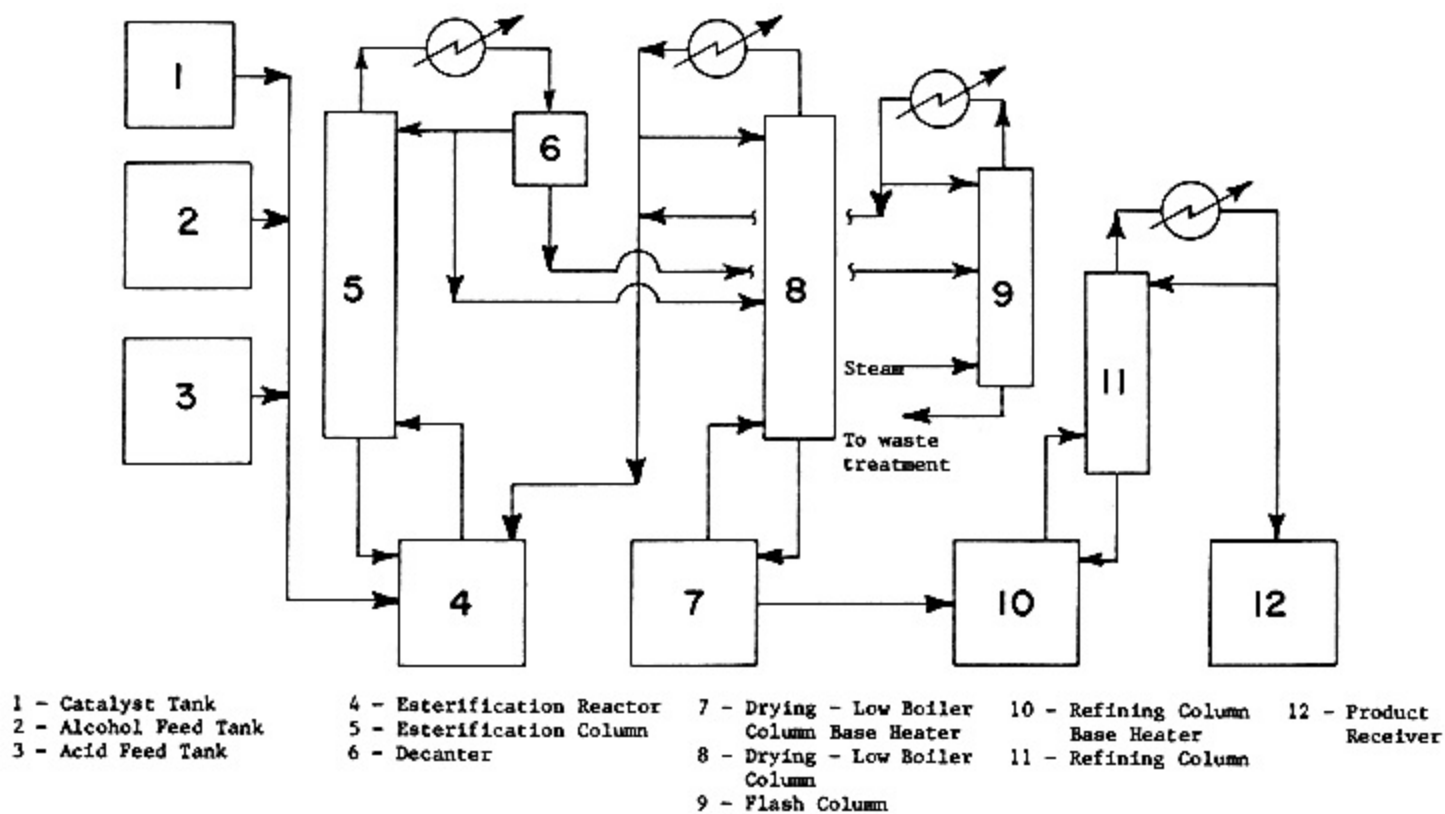


Fig. 2.
Continuous esterification: Volatile ester.

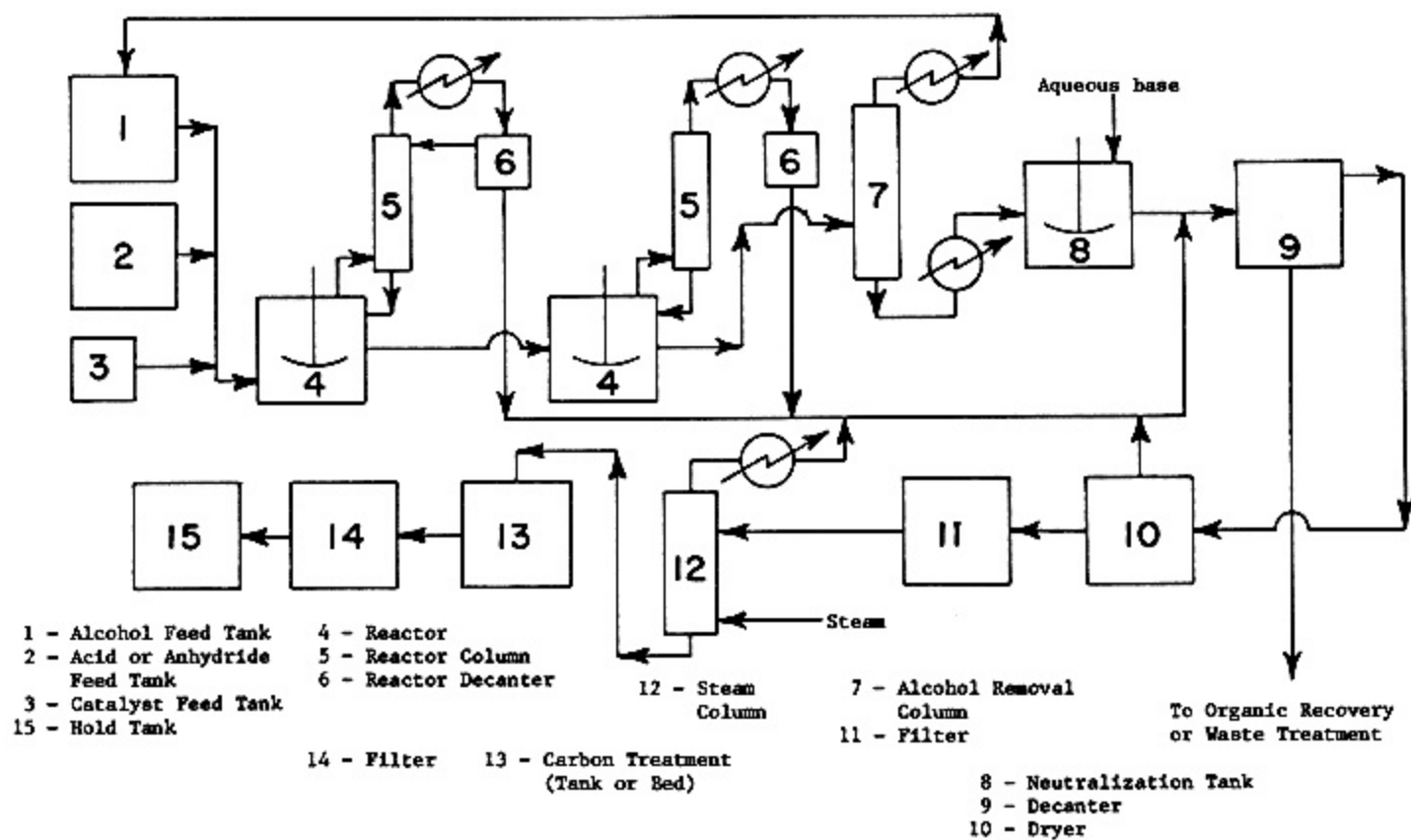


Fig. 3.
 Continuous esterification: High boiling alcohol, inert azeotroping agent.

A somewhat different scheme can be utilized for continuous production when an added azeotroping agent is used with higher boiling alcohols. This scheme is shown in Fig. 3. In this case the organic phase from the decanter is returned completely to the esterification column. Water is continuously removed and handled as previously described. Ester, some alcohol, water, and acid are removed from near the bottom of the esterification column as a sidedraw, condensed, and fed to the low boiler column. The ester is separated from the other components which are taken overhead and returned to the esterification reactor. The product is fed from the low boiler column base heater to the refining column from which it is distilled and pumped to product receivers.

Equipment similar to that depicted in Fig. 3 can be used to manufacture relatively volatile esters from anhydrides. Start-up consists of adding the anhydride to the esterification reactor and bringing it to reflux before alcohol feed is started. Once alcohol feed is started, the acid produced in the esterification reaction is removed from the top of the esterification column and stored. The ester containing some anhydride and acid are removed as a sidedraw, condensed, and fed to the low boiler column. Acid, anhydride, and some product are taken overhead on the low boiler column and returned to the esterification reactor. The product is fed from the base heater of the low boiler column to the refining column where it is distilled from any high boiling residue. Since water is not produced, the flash column is not used in this process. A requirement for this scheme is that the product be higher boiling than either the acid or anhydride. Should it be more volatile than the acid or anhydride, it would be removed from the top of the esterification column and refined on one of the other columns of the system. Acid could be removed from the esterification column as a sidedraw.

Nonvolatile Esters

General procedures are given for the preparation of relatively nonvolatile esters such as phthalates, adipates, and oleates in which the alcohol is virtually insoluble in water and can be used to remove the water of reaction (an inert water entrainer will also function for this purpose). Figure 4 shows a typical batch unit for production of these types of materials. The carboxylic acid (or dibasic acid anhydride, e.g., phthalic anhydride), excess alcohol, and catalyst are added to the reactor. The catalyst may be a strongly acidic catalyst or a metallic catalyst as previously described. Heat is applied and the reactor is brought to reaction temperature. The refluxing alcohol will remove the water of reaction as formed. It is continuously removed from the decanter and, depending on the solubility of the alcohol, sent to wastewater treatment or stored for recovery of the alcohol. A reactor column of 1520 ft of packing is usually sufficient. The reaction is monitored by withdrawing samples and analyzing for unreacted acid. When the acid concentration has been reduced to the desired level, the decanter is bypassed and the excess alcohol is distilled

from the reactor by slowly reducing the pressure of the reactor. After the alcohol is removed and stored for subsequent batches, the steam is shut off the reactor and the reactor is returned to atmospheric pressure. The material is discharged to the neutralization tank and cooled (the reactor is now ready for the next batch). The crude ester is sampled and analyzed for acid. Based on this analysis, a determined amount of dilute base is added and the tank is agitated. After settling, the organic phase is again checked to determine that it is neutral. The aqueous phase is removed and held in a tank for recovery of organic material. The wet ester is pumped to a dryer where moisture is removed at approximately 100°C and reduced pressure. After drying, the ester is filtered and fed to a column where it is contacted with steam to remove traces of alcohol. It is then pumped to the decolorization tank where it is contacted with activated carbon at 80-100°C. After decolorization, the material is filtered, transferred to hold tanks, and then to main storage after specification analysis.

A continuous process for the manufacture of the same type of product is schematically shown in Fig. 5. Alcohol and catalyst are pumped to the first reactor from their respective tanks. The alcohol is slowly brought to reflux by applying steam. The acid or anhydride feed is started at reduced setting. The reaction is allowed to proceed until an acid level typical of the second reactor under normal operating conditions is obtained. A portion of the reaction mixture is then drained to the second reactor. Agitation and heating are then begun on the second reactor. When the desired acid level is achieved in both reactors, continuous feed of alcohol, acid, and catalyst is begun. Water of reaction is continuously removed from reactor decanters and transferred to a hold tank for organic recovery or disposal through the wastewater system. The acidity of the reaction mixtures in each reactor is monitored to confirm desired levels. If the desired acid concentration is not being obtained in the second reactor, the level of the reactor can be increased to allow for a longer hold time. When the acidity of the crude reaction mixture is within limits, it is fed to the alcohol removal column which operates at a reduced pressure and at a temperature such that the major portion of the excess alcohol is removed. The condensed alcohol is returned to the alcohol feed tank and furnishes feed to the first reactor along with fresh alcohol. The alcohol removal column is controlled by reflux ratio, feed rate, and takeoff at specified base heater and top temperature settings. The column underflow is continuously removed through a cooler to the agitated tank where it is neutralized with dilute base. The crude neutralized ester and aqueous base flow continuously to a settling tank. The aqueous phase is removed to wastewater treatment. The product layer continuously overflows to a hold tank which feeds a dryer operating at reduced pressure. The dried product is filtered to remove any inorganic salts and fed to a stripping column where it is treated with steam at reduced pressure to remove the last traces of alcohol. The steam-stripped product is then decolorized with activated carbon, filtered, and transferred to analysis tanks where quality is confirmed before placing the material into storage.

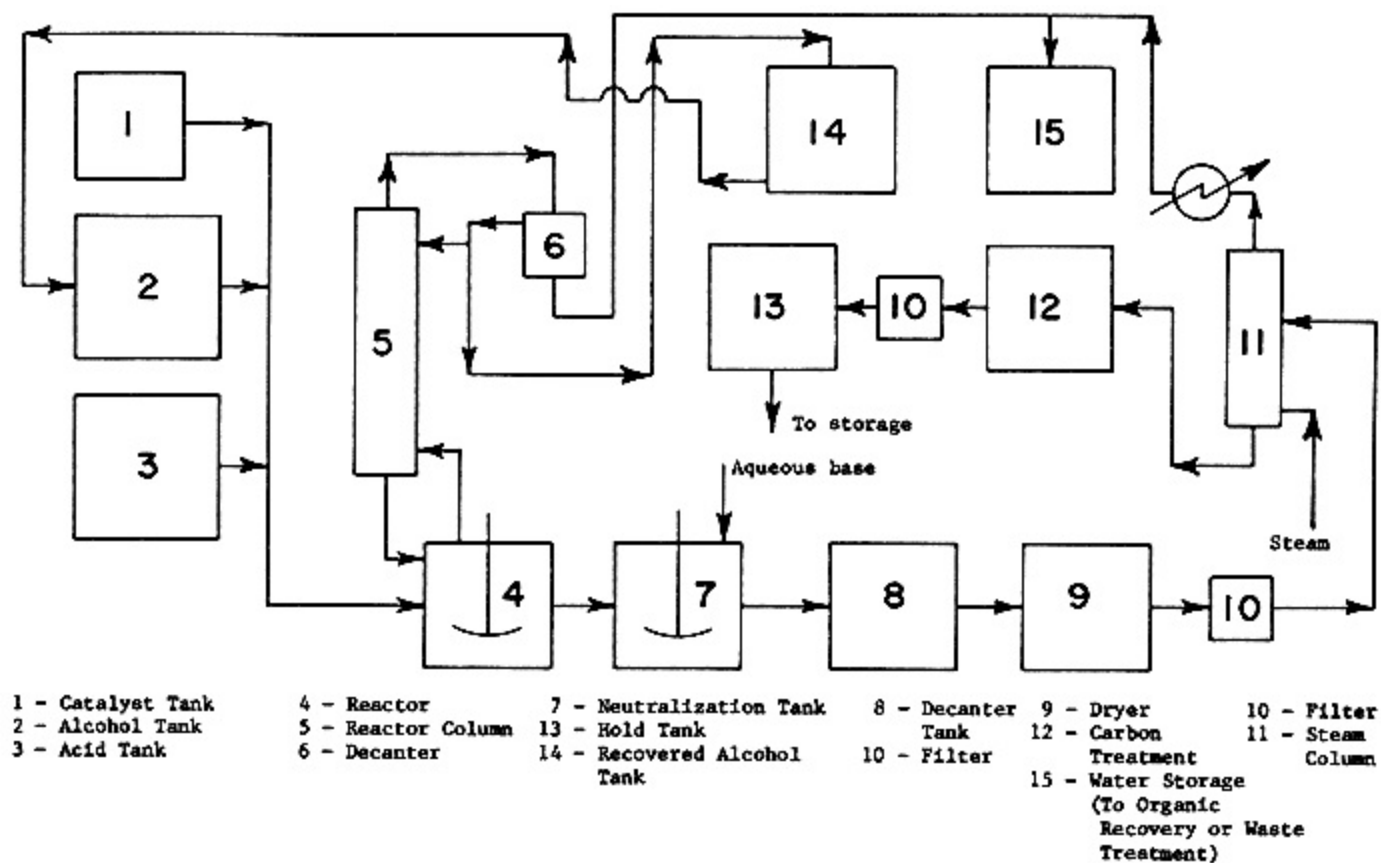


Fig. 4.
Batch esterification: Nonvolatile ester.

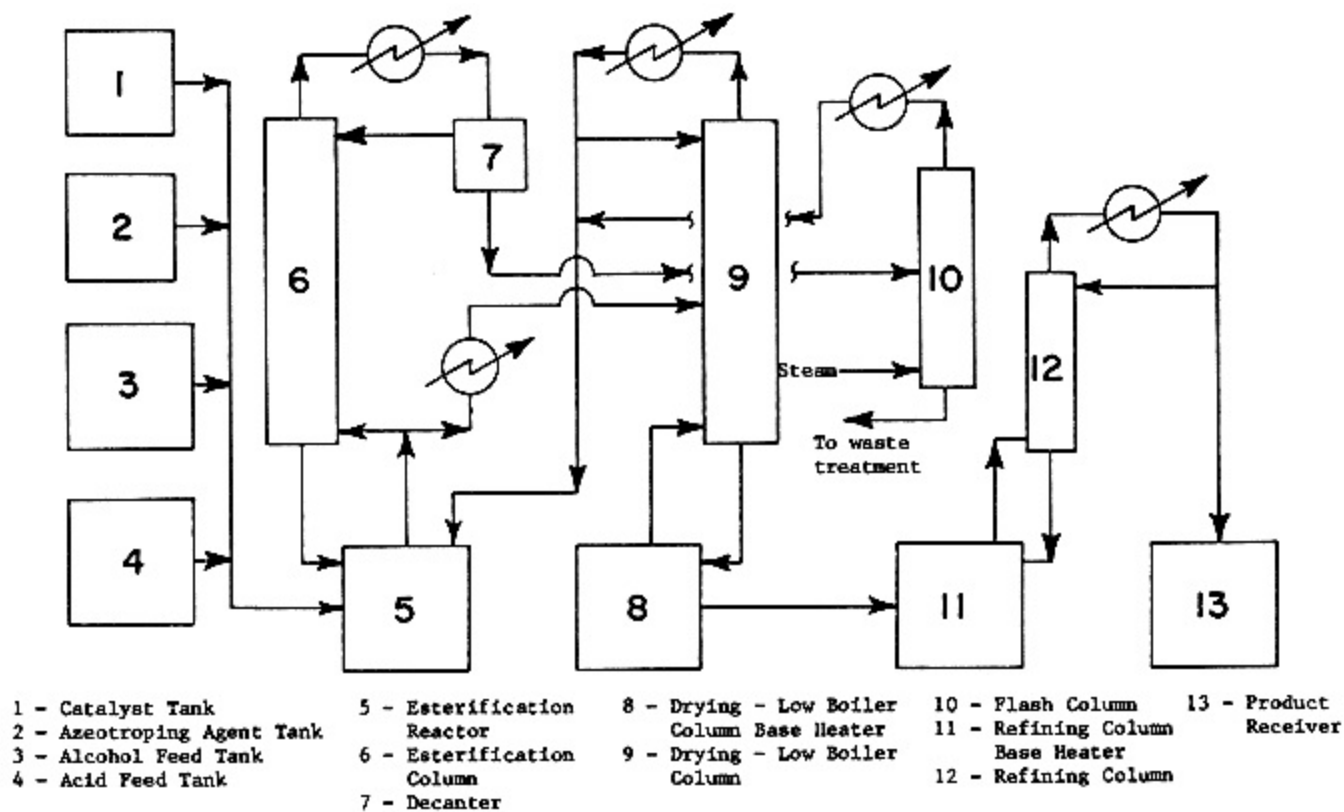


Fig. 5.
 Continuous esterification: Nonvolatile ester.

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Fischer-Tropsch Synthesis

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Historical Background and Importance of the Fischer-Tropsch Synthesis

The discovery of Franz Fischer, Hans Tropsch, W. Ter-Nedden, Th. Bahr, K. Meyer, and O. Roelen of the catalytic hydrogenation of carbon monoxide is known today as the "Fischer-Tropsch (FT) Synthesis." In 1922, intensive laboratory work was initiated by the former Kaiser-Wilhelm-Institute. Then, in 1934, Ruhrchemie AG, as general licensor, transferred the synthesis to the industrial scale. Between 1936 and 1945, Ruhrchemie licensed 12 FT plants with a total capacity of ~ 1 million tons per year of FT products, mainly gasoline and diesel oil. During World War II, Germany produced millions of tons of FT products.

After the war, work on FT synthesis was temporarily prohibited in Germany. As a consequence, the first newer developments took place in 1954. The best known was "ARGE-High Capacity Synthesis," jointly developed by a team (Arbeitsgemeinschaft) consisting of Ruhrchemie AG and Lurgi GmbH. In 1954 this process was licensed to the South African Coal, Oil and Gas Corp. Ltd. (Sasol) in South Africa and became the first step toward a coal refining plant. The progress reached in 10 years of development work is illustrated in Fig. 1.

Work done by the British Fuel Research Station after 1934 was continued in the postwar

period by C. C. Hall at the Warren Springs Laboratory (Stevenage). In the United States, different laboratories investigated FT synthesis after 1943. At the end of the war, work was mainly conducted by the

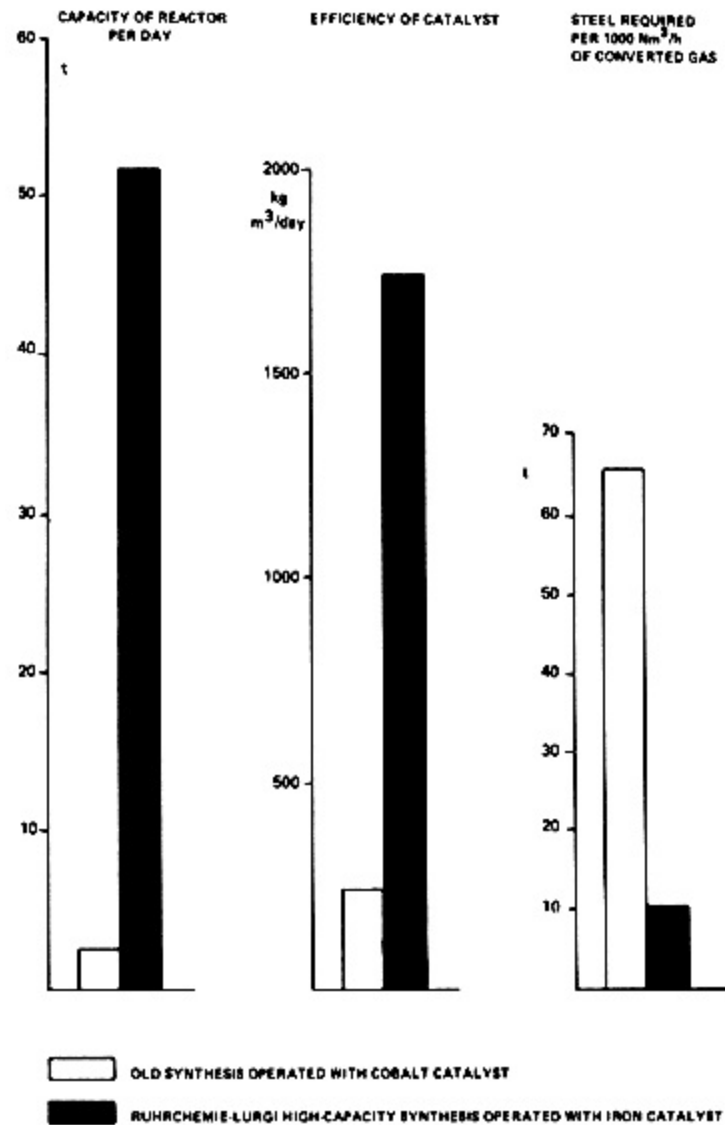


Fig. 1.
Efficiency of ARGE-Fischer-Tropsch Synthesis [1].

Bureau of Mines (R. B. Anderson). Other process variants were developed by Hydrocol at Brownsville, Texas (fluidized bed process; a large plant for the production of 365,000 tons of FT products per year was in operation between 1950 and 1953) and by the Kellogg Co. (after 1947 as the entrained bed process). The Kellogg process was also licensed to Sasol and developed by Sasol to industrial technical maturity (later designated as the "Synthol process").

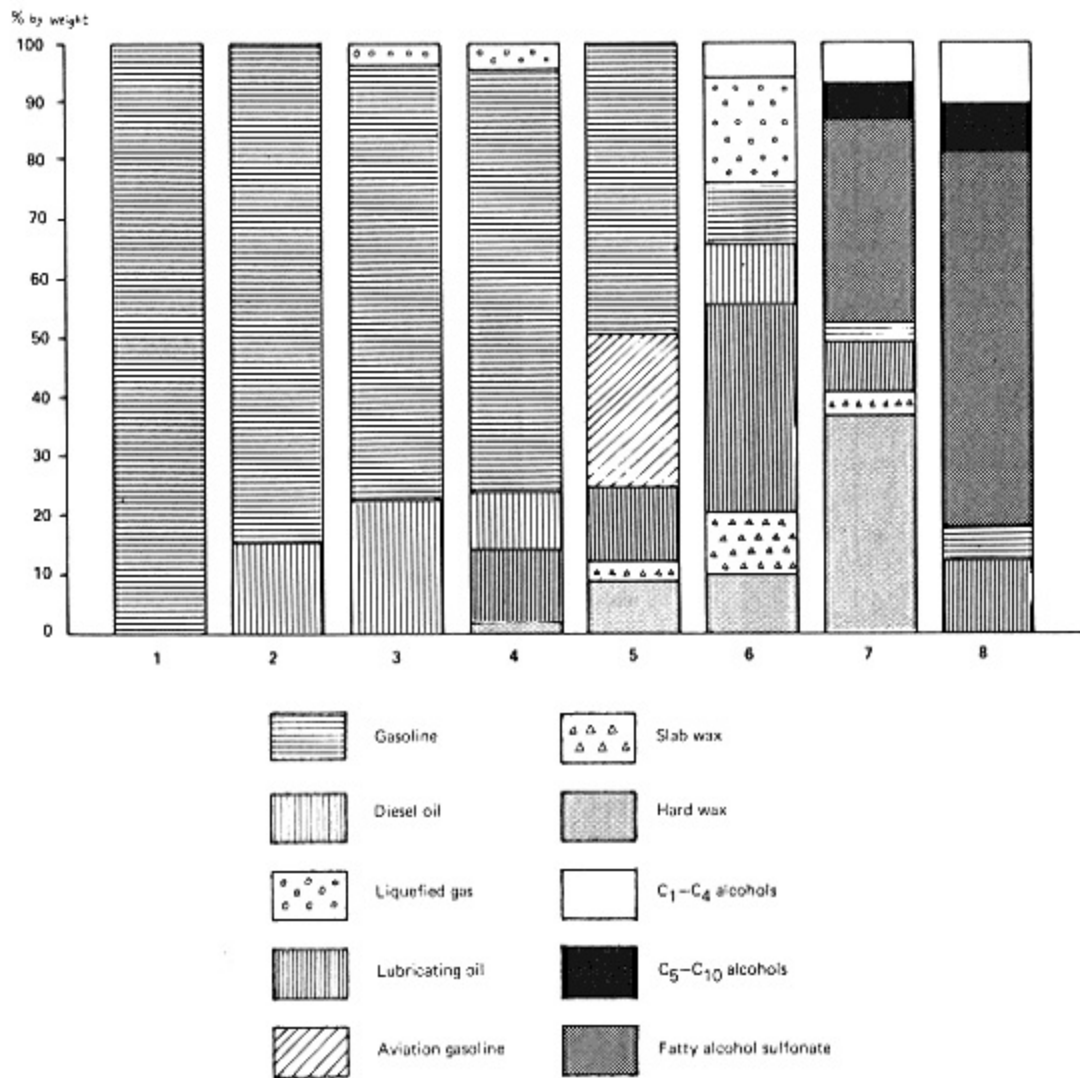


Fig. 2.

The most important possibilities for working up Fischer-Tropsch products [1].

Originally FT synthesis was developed for the production of motor fuels via CO hydrogenation. In spite of this aim, by-products of FT production gained importance as chemical feedstocks even in the first years of industrial production. These included the olefinic components of FT product mixtures, which were the feedstock for the first oxo plant in the world (1943 on the Ruhrchemie plant site) for the production of detergent alcohols. A separate 15,000 tons per year plant produced lubricants by polymerization of FT olefins. If required, the saturated hydrocarbons of FT synthesis were chlorinated, sulfochlorinated, oxidized, or nitrated and converted to the desired

derivatives. For example, in 1944, 100,000 tons of FT products were converted to synthetic fatty acids by oxidation and 70,000 tons by sulfochlorination to detergents.

Such oxygen-containing compounds as aldehydes, alcohols, and ketones, present in the aqueous phase after the FT reaction, were also isolated at an early stage of FT synthesis and were used for downstream syntheses. The same was true for products boiling above 320°C, which were worked up to high-grade paraffinic hydrocarbons and waxes.

At present, Sasol operates the only large-scaled FT plant, and the focal point of its product range is still the production of motor fuels. Nevertheless, considerable parts of the product are used chemically and are converted to intermediates and to final products.

Some of the working-up alternatives for FT products, investigated in more detail, are shown in Fig. 2.

2

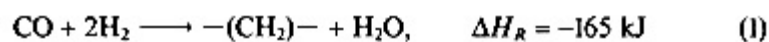
General Aspects of the FT Synthesis

2.1

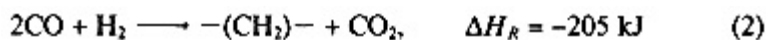
Stoichiometry and Thermodynamics

The hydrogenation of carbon monoxide in the presence of cobalt-, iron-, or ruthenium-containing catalysts produces alkanes and alkenes, predominantly of linear structure, ranging from methane to polymethylene as long-chain hydrocarbons. Alcohols, aldehydes, ketones, acids, and esters are formed as by-products, representing around 5% of the total primary product. At high synthesis temperatures, aromatic hydrocarbons are formed in small amounts [2].

In the presence of cobalt or ruthenium catalysts, hydrocarbon formation is generally accompanied by the production of water as an oxygenated product:



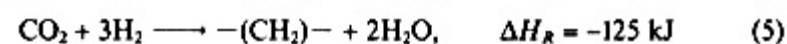
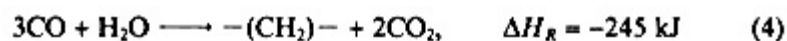
In the presence of iron catalysts and, generally, with increasing synthesis temperature, carbon dioxide formation (as an oxygenated product) increases in importance:



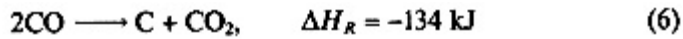
Equations (1) and (2) are linked via the shift conversion equilibrium:



On combining Eqs. (1) to (3), two equations result:



Equation (4) describes hydrocarbon synthesis from carbon monoxide and water vapor (Kölbel-Engelhardt synthesis) [3], and Eq. (5) the hydrogenation of carbon dioxide via the reverse shift conversion. Carbon deposition (Eq. 6, Boudouard equilibrium) and methane formation (Eq. 7) are undesired side reactions of the FT synthesis:



To summarize, the formation of hydrocarbons may be expressed as a combination of part of Eqs. (1) to (3), depending on the reaction conditions and the properties of the catalyst. The maximum yields can be attained when hydrogen and carbon monoxide are introduced in the same ratio as they are converted (feed ratio = consumption ratio). For each type of synthesis or catalyst an optimum feed ratio can be chosen which may either be rich in hydrogen (cobalt and ruthenium catalysts) or rich in carbon monoxide (iron catalysts). The maximum attainable yields of hydrocarbons for some different feed and consumption ratios are listed in Table 1 [4].

Due to the different consumption of CO and H₂, the synthesis gas conversion is generally expressed as (CO + H₂) conversion. The yield of hydrocarbons may be calculated using the stoichiometric equations by establishing the composition of feed gas and tail gas via volume contraction [5, 6].

The main reaction and the side reactions of the FT synthesis possess negative reaction enthalpies. Depending on reaction conditions and catalyst, between 2450 and 3050 kJ are liberated per cubic meter of converted synthesis gas when either water (Eq. 1) or carbon dioxide (Eq. 2) is formed. The enthalpy of the total reaction increases with increasing concentration of carbon monoxide in the feed gas and with increasing concentration of carbon dioxide in the tail gas. The temperature dependence of the reaction enthalpy is minor. With increasing chain length of the resulting hydrocarbons, the enthalpy per mole (CH₂) product nears a limiting value [7].

The standard free reaction enthalpies ΔG_R° for the main reactions under FT conditions are listed in Table 2. Additionally, the inversion temperatures T_i ($\Delta G_R^\circ = 0$) are presented, and they allow the temperature range in which the single reaction may contribute thermodynamically to product formation to be derived.

TABLE 1 Maximum Attainable Yields of Hydrocarbons (g/m³ synthesis gas)

Consumption Ratio, H ₂ :CO	Feed Ratio		
	1:2	1:1	2:1
1:2	208.5	156.3	104.3
1:1	138.7	208.5	138.7
2:1	104.3	156.3	208.5

TABLE 2 Standard Free Reaction Enthalpies and Inversion Temperatures of Some Reactions Possible under FT Reaction Conditions [8]: ΔG° (250°C, 1 bar), Ti ($\Delta G^\circ = 0$, 1 bar)

Reaction	ΔG° (kJ/mol)	Ti (°C)
(1)	-26	346
(2)	-83	393
(3)	-20	740
(4)	-66	427
(5)	-8	330
(6)	-80	700
(7)	-91	636

To calculate the product composition at thermodynamic equilibrium, procedures based on linked (simultaneous) equilibria [9, 10] have been developed.

2.2

Kinetics and Mechanism

The composition of the reaction products of FT synthesis (ratio of alkanes to alkenes, chain length distribution, formation of water or carbon dioxide) is kinetically controlled and does not correspond to the composition predicted by thermodynamics. According to the latter, the main products should consist of methane and carbon dioxide [7]. The hydrogenation of carbon monoxide passes through a complex system of consecutive and parallel reactions on the way to the final products. The first step is the simultaneous chemisorption of hydrogen and carbon monoxide on metallic sites of the catalyst surface. Hydrogen is most likely chemisorbed dissociatively, whereas carbon monoxide is bound to the catalyst metal (Co, Fe, or Ru) by a carbonmetal bond. This causes weakening of the CO bond, facilitating reaction with hydrogen atoms. The consecutively formed products are assumed to have either enolic or aldehydic structures capable of inter- or intramolecular abstraction of water followed by additional interaction with hydrogen and carbon monoxide. The hypothetical primary complexes, the structures of which have not yet been proven conclusively, may stabilize by desorption or by hydrogenation after having passed through a sequence of consecutive reactions. Alkenes, alcohols, aldehydes, or ketones (as reactive products) may reenter the consecutive or constructive reactions [4, 1114].

As a consequence of the complex path of reaction and of the plurality of reaction parameters (temperature, pressure, synthesis gas composition, catalyst, mass and heat transfer), it has not been possible to establish a generally valid expression for the rate of reaction. However, for certain defined catalysts and reaction conditions, reaction rate constants have been evaluated [15, 16]. In the presence of cobalt catalyst, the rate of reaction is proportional

to the ratio of the partial pressures $P_{H_2}^2/P_{CO}$. In the presence of iron catalysts, which catalyze the shift conversion, the rate of reaction nears first order with respect to the hydrogen partial pressure, and nears zero order with respect to the carbon monoxide partial pressure. Water vapor and carbon dioxide tend to decrease the rate of reaction, a fact often taken into account by correction factors in reaction rate expressions [17]. For Co, Fe, or Ru catalysts, the apparent activation energies cover the range from 85 to 110 kJ/mol, thereby indicating that transport reactions to or from the catalyst surface are unlikely to be rate-determining steps.

2.3

Possibilities of Influencing the Reaction Path

Temperature, pressure, and synthesis gas composition are the main factors used to influence the reaction pathway by thermodynamic or kinetic means.

The temperature of the synthesis varies with the nature of the catalyst and with the type of heat removal applied in the process. Common ranges are 180–210°C for cobalt catalysts and 220–350°C for iron catalysts [4]. The synthesis of polymethylene with ruthenium catalysts is carried out at 100–120°C [18]. The lowest applicable reaction temperature is limited by the catalyst activity and by the tendency of the catalytically active material to form soluble or vaporizable carbonyls (depending on the carbon monoxide partial pressure). The upper limit of the practical temperature range results from an increase in the side reactions (methanation, Boudouard equilibrium) which reduce the yield of value products or which cause catalyst activity decay, e.g., by hot spots. Increasing the temperature results in the following reactions:

- Reaction rate of main and side reactions increases
- Average molecular weight of the products decreases
- Formation of branched chain hydrocarbons increases
- Formation of oxygen-containing compounds increases

At a fixed temperature the increase in pressure is limited mainly by technical or economic aspects, and by the tendency of catalyst metals to form carbonyls. Increasing the pressure results in the following effects:

- Average molecular weight of the products increases
- Formation of methane is reduced
- Specific conversion of the catalyst and the service life of the catalyst are augmented
- Cobalt catalysts (5–15 bar) are more sensitive to pressure than iron catalysts (10–40 bar).

The composition of the synthesis gas, which must be adapted to the consumption ratio, influences the reaction rate as well as the product compo-

sition. Increasing the hydrogen partial pressure results in the following reactions:

- Formation of methane increases
- Average molecular weight of the products decreases
- Formation of alkenes decreases
- Reaction rate increases

An increase in space velocity or a reduction in residence time causes a decrease in conversion and side reactions, respectively. As a consequence, along with improved mass and heat transfer, the average molecular weight of the products decreases together with an increase in the formation of alkenes and oxygen-containing by-products.

The combination of temperature, pressure, synthesis gas composition, and space velocity has to be arranged individually within the limits set by the mode of reaction and by the properties of the catalyst [19].

3 Industrial Processes

3.1 Generation and Purification of Synthesis Gas

Synthesis gas for FT synthesis consists mainly of hydrogen and carbon monoxide. Methane, carbon dioxide, and nitrogen may be present in minor amounts. The type of synthesis gas generated and the gasification feedstock are insignificant for the synthesis. The gasification of crushed or powdered carbonaceous fossil materials is carried out via appropriate processes (Lurgi pressure gasification or Koppers- Totzek gasification [20]). At present, substantial improvements of these established processes are under development with the aim of operating under increased pressures (4080 bar), increasing specific throughputs, and being independent of the coal quality [21, 22]. Lurgi pressure gasifiers are used in the expanded plants of Sasol III with a synthesis gas production capacity of 45,000 m³/h raw gas per unit [8]. The generation of synthesis gas by steam reforming of methane or other hydrocarbons has no importance for FT synthesis except that the methane formed during FT synthesis is used.

Cobalt- or iron-based FT catalysts are sensitive to poisoning by sulfur or sulfur compounds (H₂S, COS, mercaptans), so that careful purification and desulfurization of the raw gas is necessary for smooth synthesis and an adequate catalyst service life. Impurities and most of the carbon dioxide can be removed from the raw gas by extraction with cold methanol (Rectisol process).

Table 3 summarizes the compositions of a raw gas (Lurgi pressure gasification) from coal and the purified gas.

TABLE 3 Compositions of Raw and Purified Gas for FT Synthesis (Sasol I)
[8]

	Raw Gas (mol%)	Purified Gas (mol%)
Aromatics	0.03	
Alkanes C2+	0.28	
Alkenes C2+	0.12	
CH ₄	9.36	12.3
CO ₂	28.2	0.66
CO + H ₂	61.2	86.0
N ₂ ,Ar	0.71	0.88
H ₂ S	0.11	
COS	0.01	

Sulfur is removed until less than 0.05 ppm remains. Tarlike and resin-forming substances are scrubbed out of the raw gas. Partial recovery yields products of value (see Section 4). A part of the purified gas can be subjected to shift conversion to yield a gas with the desired H₂/CO ratio.

3.2 Preparation and Activation of Catalysts

Cobalt catalysts have played a significant role during the development of FT synthesis. However, at present they have no industrial application.

All iron-based FT catalysts contain alkali metal compounds, predominantly in the form of K₂O or K₂CO₃, as energetically active promoters. The electron-releasing properties of the alkali metal ions enhance the chemisorption of carbon monoxide to metallic iron, thus accelerating its reactions (synthesis, conversion, carbon deposition). With respect to iron, the concentration of alkali metal compounds varies between 0.2 and 5.0 parts by weight depending on the type of preparation and the mode of use of the catalyst.

Besides energetically active promoters, FT catalysts contain additives which influence the structure of the iron and/or the structure of the catalyst surface (structural promoters). They mainly consist of oxides which are difficult to reduce (e.g., SiO₂, Al₂O₃, ThO₂, MgO, CaO). They create lattice distortions and stabilize the structure toward recrystallization by thermal or chemical effects. Carriers may also serve as structural promoters.

The combination of iron and promoters to yield the catalyst is accomplished by precipitation or by thermal homogenation (sintering, fusing). Precipitated catalysts in general possess relatively large surface areas and therefore are highly reactive, favoring a low synthesis temperature (220°C). Low surface area sintered or fused catalysts are restricted to reaction temperatures >>280°C [19].

The catalyst for the ARGE process (see Section 3.3.1) has the composition 100 Fe-5 K₂O-5 Cu-25 SiO₂ parts by weight. Its preparation is carried out by the addition of boiling sodium carbonate solution to a boiling iron-copper-

nitrate solution with intense mixing. The suspension is filtered, and the filter cake is freed from sodium ions by washing thoroughly before being impregnated with potassium silicate solution. The excess of potassium ions is lowered to the desired level by washing with dilute nitric acid solution. The shaped and dried material is reduced by hydrogen at 230°C until 25% of the iron is in the metallic state and 45% of the iron is converted to Fe^{2+} . Catalysts for the slurry phase process (see Section 3.3.3), which generally do not possess a support, are prepared in an analogous manner.

Catalysts for the entrained bed process (see Section 3.3.2) are prepared by fusing iron oxide (Fe_3O_4) together with promoters in an electric arc furnace at 1500°C. Magnetite is formed as a stable modification and as a solvent for the promoting oxides. The cooled melt is broken, milled, and screened, yielding a particle size between 50 and 150 μm . Reduction of the catalyst by hydrogen takes place in a fluidized bed for 50 h at 400°C. More than 95% of the iron is reduced to the metallic state. During the reduction process the catalyst becomes a porous structure which is stabilized by the promoting oxides (Si, Al, or Mg oxides) [4]. The processes for preparing fused catalysts and ammonia synthesis catalysts are comparable.

3.3 Process Description and Working Method

During the 50-year history of the Fischer-Tropsch synthesis [19], several process technologies have been developed. Besides pressure, temperature, syngas ratio, and catalyst, their main characteristics are the different chemical engineering techniques for exothermal heat removal. These processes are:

- Fixed-bed reactors with fixed catalyst beds, through which syngas flows [4, 23, 25]
- Entrained fluid-bed or fluidized-bed reactors with catalysts moved by syngas [24, 25]
- Liquid-phase reactors with fixed or agitated catalysts [4, 25, 26]

From the large number of potential process technologies, only a fraction has reached the semitechnical stage. Only two processes have been successful on an industrial scale and are operating at the South African Coal, Oil and Gas Corp. (Sasol): the fixed-bed ARGE process developed by Ruhrchemie-Lurgi and the entrained-fluid-bed process developed by M. W. Kellogg Co. using a powdered iron catalyst swept along by the gas stream. Therefore, both process technologies are, besides fluidized bed and liquid-phase synthesis, the focal points of the following discussion.

3.3.1 Gas-Phase Process

The first production units, which went into operation in 1936, were equipped for normal pressure synthesis with lamella reactors. These reactors, with

dimensions of 2.5 m in height, 1.5 m in width, and 5 m in length, had a 10 m³ catalyst content. The reactor shell was a rectangular, iron-plated tank. The reaction chamber was occupied by a bundle of 630 tubes and 555 vertical iron plates which were arranged parallel to each other at a distance of 7 mm (cf. Fig. 3).

The plates served to transfer the heat of reaction to the system of horizontal cooling tubes in which pressurized water was circulating. The uniform filling of the narrow interspaces of the lamella bundle demanded considerable care and expense. Removal of the spent catalyst, which becomes solid during the catalyst service life due to high boiling reaction products and deposits of Boudouard carbon, was even more difficult. In spite of the large cooling surface [4 m² per converted m³ (ntp) syngas], heat removal was unsatisfactory. Carbon deposition and grain degradation resulted as a consequence of local superheating.

An essential improvement in the removal of heat of reaction, in comparison to the lamella reactors, was connected with the development of twin tube reactors built for a pressure of 12 bar and temperatures below 220°C. The catalyst was placed in the space (a distance of 10 mm) between two concentric tubes (cf. Fig. 4).

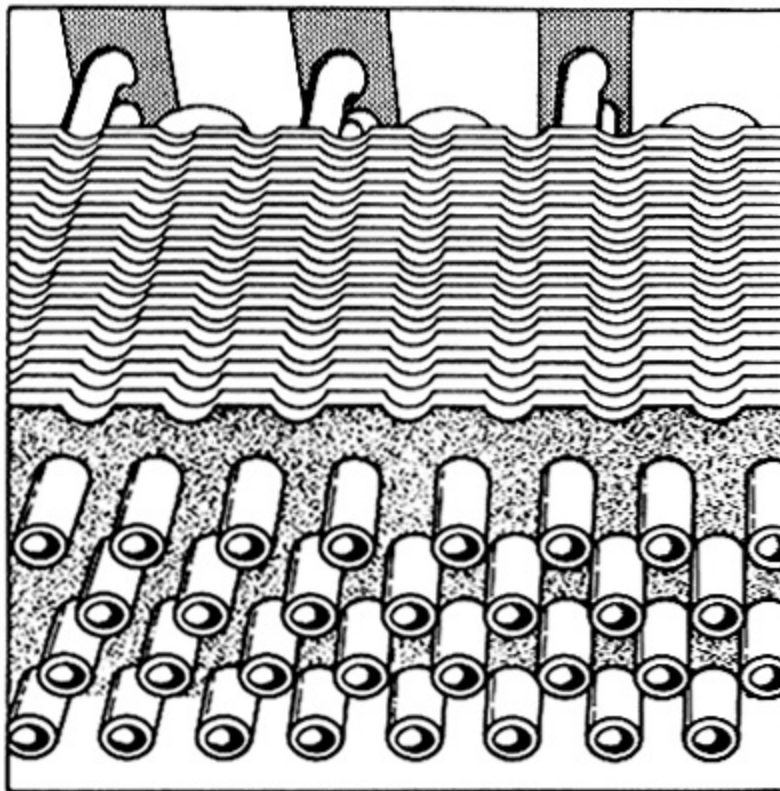


Fig. 3.
Section of a lamella bundle [25].

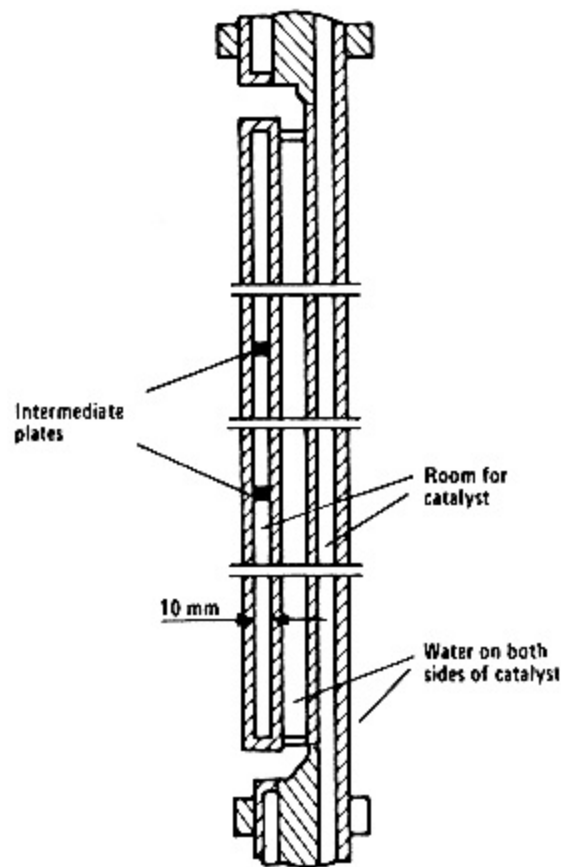


Fig. 4.
Single twin tube.

The spaces outside the outer tube (44 mm diameter) and inside the inner tube (24 mm diameter) were filled with pressurized water (~ 24 bar) for heat removal. Industrial reactors contained up to 2044 twin tube aggregates (4.5 m length), the total catalyst volume being 10 m³. Although they possess about 10% less specific cooling surface compared to the lamella reactor, heat transfer was essentially improved and enabled the typical superheating problems to be almost totally eliminated. Reactors of this type were used for medium pressure synthesis with cobalt and iron catalysts.

On the basis of these good results, intensified efforts (Ruhrchemie-Lurgi) concerning the heat removal problem led to the new ARGE high capacity reactor. As a result of this development, the reactor had a 40-m³ catalyst volume with 2052 tubes of 46 mm diameter and 12 m lengths surrounded by pressurized water (cf. Fig. 5).

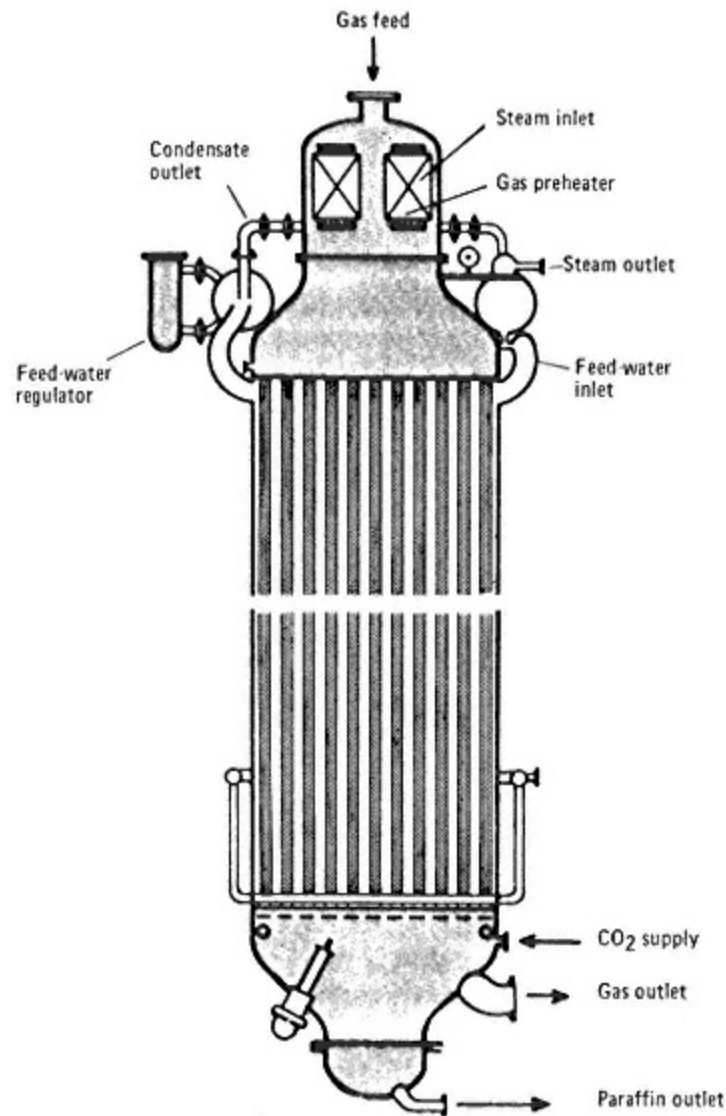


Fig. 5.
ARGE high capacity reactor [25].

Compared to the previous methods, an essential improvement in heat transfer from the catalyst charge to the cooling jacket could be reached by increasing the gas velocities (above 1 m/s relative to normal conditions) and operating with the gas recycle in the turbulent flow region [27]. As confirmed by Sasol's industrial operation over the previous decades, the high capacity reactors have enjoyed a high degree of reliability coupled with high reactor output (see Table 4).

TABLE 4 Data from Various Fixed-Bed Reactors

	Lamella Reactor	Twin Tubular Reactor	Tubular Reactor. ARGE Process
Depth of catalyst layer (mm)	7	10	46
Length of catalyst layer (mm)	2,500	4,550	12,000
Operating pressure (bar)	0.3	712	2030
Operating temperature (°C)	180195	180215	220260
Cooling surface m2/m3 (ntp) CO + H2 converted	4,000	3,500	230
Fresh gas feed (GHSV)	70100	100110	500700
Daily production single stage per m3 catalyst (kg C2+)	190	210	1,250

Used efficiently, one catalyst charge lasted about a year. The process diagram of high capacity synthesis with iron catalysts is shown in Fig. 6.

At the beginning of the reaction, the temperature starts at 200230°C with a pressure of 2325 bar. The purified, compressed syngas [fresh gas charge 500700 m3 (ntp)/m3 catalyst · h] mixed with recycling gas is fed to the top of the catalyst bed in a ratio of about 1:2.5. High boiling products are separated on leaving the reactor, and after passing a multiclone and a heat exchanger, the gas reaches the condenser. In the latter, low boiling products, water of reaction, and oxygen-containing products are separated. The tail gas is separated into two streams: recycle gas and residual gas, which pass an oil scrubbing tower, a charcoal aggregate, and a Rectisol plant for separating gasoline and gas. In a two-stage process the residual gas (of the first stage) is fed, without product isolation, to the second stage. To maintain a 6570% syngas conversion over a period of 912 months, the temperature is increased to 250°C.

Process conditions of several commercial FT plants and typical product compositions are presented in Tables 5 and 6.

As shown in Tables 5 and 6, the gas-phase fixed-bed process exhibits exceptional flexibility. However, these data should not be understood to demonstrate a limitation of the product composition, but rather they are examples of adoption to prevailing conditions and to typical catalysts.

3.3.2 Entrained-Bed and Fluidized-Bed Synthesis

Kellogg Company (USA) successfully erected an entrained-bed plant (Synthol process) based on previous process developments [28]. Since 1956 entrained-bed plants with a capacity of around 80,000 tons/year have been operating at the South African Coal, Oil and Gas Corp. (Sasol) for the (economic) production of coal-based gasoline. The operation of two enlarged, new entrained-bed plants (Sasol II and III) with a capacity of 2 million tons/year each has begun. The entrained-bed reactor and the main process lines

are presented schematically in Fig. 7.

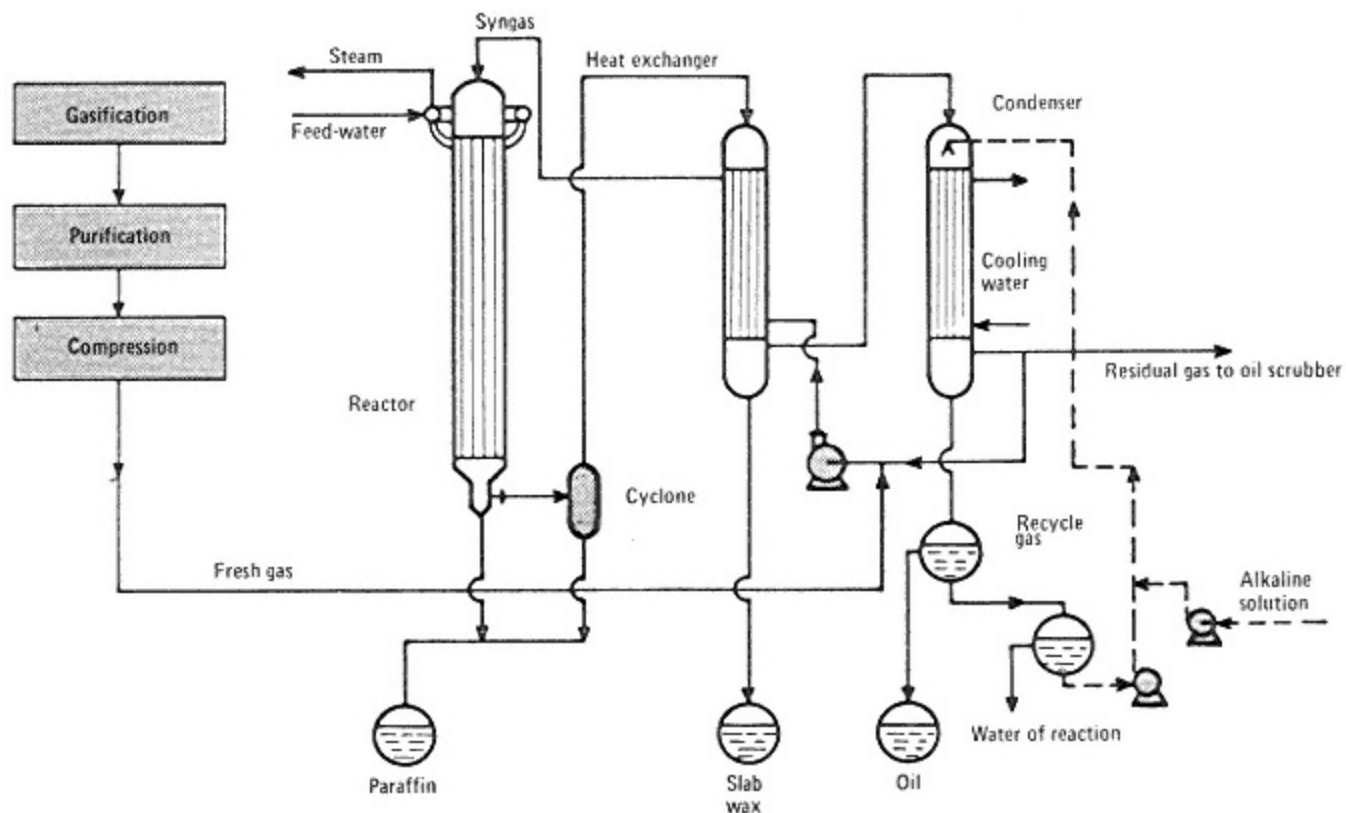


Fig. 6.
Process diagram of high capacity synthesis with iron catalysts [25].

TABLE 5 Operating Conditions of Commercial FT Syntheses Plants Using the Gas-Phase Fixed-Bed Process during the Development Period

Features of Process	Cobalt Normal Pressure Synthesis	Cobalt Medium Pressure Synthesis	Iron Medium Pressure Synthesis	ARGE High Capacity Synthesis
Year	1936	1939	1952	1955
Process conditions:				
Pressure (bar)	0.3	712	11	2325
Temperature (°C)	180195	180210	190230	220250
H ₂ /CO ratio in fresh gas	2	2	1.25	1.32
Recycle/fresh gas ratio	No recycle	Normally no recycle	2	2.5
No. of stages	2	3	2	12
Fresh gas load (m ³ (ntp)/m ³ · h)	70100	100110	100110	500700
Type of heat removal	Water-cooled lamella	Water-cooled twin tube	Water-cooled twin tube	Water-cooled tubes
Catalyst:				
Composition (parts by weight)	100 Co, 8 MgO, 5 ThO ₂ , 200 kieselguhr	100 Co, 8 MgO, 5 ThO ₂ , 200 kieselguhr	100 Fe, 5 Cu, 5 K ₂ O, 25 SiO ₂	100 Fe, 5 Cu, 5 K ₂ O, 25 SiO ₂
Lifetime (months)	46	67	12	912
Reactors:				
Catalyst charge (m ³)	10	10	10	40
No. of tubes		2,044	2,044	2,052
Dimensions of tubes H mm × D mm		4,450 × 10 ^b	4,450 × 10 ^b	12,000 × 46
Amount of catalyst per tube (L)		4.9	4.9	20
Production capacity per reactor (tons C ₂ +/day)	1.9	2.5	2.5	50

^aDimensions of reactor: 1500 mm width × 2500 mm height × 5000 mm length.

^bInner tube 21 × 24 mm; outer tube 44 × 48 mm.

TABLE 6 Typical Product Compositions of Several Commercial FT Synthesis Plants

Features of Process	Cobalt Normal Pressure Synthesis ^b	Cobalt Medium Pressure Synthesis ^a	Iron Medium Pressure Synthesis ^b	ARGE High Capacity Synthesis ^c
Average product composition alkanes/alkenes (parts by weight):				
C1/C2 hydrocarbons	ND ^d	ND ^d	5/	7/
C3/C4 hydrocarbons	8/6	6/4	2/6	5/5
Fractions: 30165°C	29.5/17.5	19.5/6.6	4.1/8.7	8.5/8.5
165230°C	14/3	21.5/2.5	2.4/3.8	5/3.5
230320°C	10/1	11/2	8/7	7.6/4.4
320460°C	8/	17/1	16/	23/
>460°C	3/	10/	37/	18/0
Oxygen-containing compounds				4
Charge (m ³ (ntp)/m ³ cat · h)	70100	100110	100110	500700
Conversion (CO + H ₂), %	9095	9095	85	73
Yield (g C ₂ +/m ³ (ntp) CO + H ₂ feed)	150160	150160	170	140

^aThree-stage process.

^bTwo-stage process.

^cSingle-stage process.

^dNot determined.

The fine powdered catalyst is rapidly moved by syngas. The temperature range lies between 300 and 350°C, with a pressure of 2023 bar. In an entrained-bed reactor (30 m height, 2 m diameter), about 135 tons of iron catalysts are recycled. About 6000 tons of catalyst are moved every hour with a fresh gas load of 90,000–100,000 m³ (ntp) and double recycle gas (about 190 kg catalyst per m³ syngas). In the upper noncooled region of the reactor, the reaction starts with a partial conversion of syngas (temperature of gas 160°C, temperature of catalyst 350°C). The temperature of the mixture of catalyst and gas increases as the reaction progresses and must be cooled by a system of cooling tubes with oil circulation [29]. The reaction area above the cooler makes it possible to achieve almost total CO conversion. The temperature is limited to 350°C via a second cooler. The catalyst, products, and residual gas leave the top of the reactor, and via connected cyclones the catalyst dust is deposited, filling the ascending tube. Syngas is introduced at several points in order to loosen the catalyst to make it suitable for recycle to the synthesis. The residual gas passes an oil scrubbing tower followed by a gasoline and gas scrubbing stage where small amounts of catalyst and high boiling products are separated. Most of the purged gas returns to the synthesis (internal recycle) and the rest is used for gas reforming (external recycle) or for low temperature separation, where hydrogen and ethylene are recovered, or as fuel gas.

A diagram of the gas flow as well as quantity and composition of gases from Sasol's entrained-bed synthesis are presented in Fig. 8.

The uniformity of the catalyst recycle is very important for process reliability and a satisfactory lifetime of 45 weeks for a catalyst charge. Especially disadvantageous are the marked formation of higher molecular weight products (blockade of cooling tubes), and the destruction and increased carbon formation on the catalyst. Definite improvement in the catalyst could be achieved via stepwise improvement and development leading to mechanically resistant, alkali-treated, fused iron catalyst based on magnetite (Fe₃O₄). Further progress could stem from an exact study of the reduction conditions. A lowering of CO partial pressure (89 vol.%) and an increase of the H₂/CO ratio to about 6:1 have led to extensive repression of the Boudouard reaction (coke deposits) at 300–350°C, which favors the formation of short-chain products.

Table 7 summarizes the average selectivity of the industrial entrained-bed process together with the reaction conditions.

The main product is gasoline. About 75% by weight of the total product spectrum consists of auto gasoline [31] (cf. Table 8) if a polymerization or alkylation of the gaseous olefins (C₃, C₄) and a blending of hydrocarbons from the coal gasification and ethanol from the reaction water are possible.

The less successful fluidized-bed process (Hydrocarbon Research Inc., Hydrocol process) shall only be briefly mentioned [25]. In 1950, after the end of research in Brownsville, Texas, an industrial plant for the production of 360,000 tons/year of hydrocarbons was

erected. Because of several technical problems, operation was unsuccessful. Stanolind took over the plant in 1954 and, after reconstruction, began the production of petrochemicals (i.e., primary alcohols, aldehydes, ketones, esters, and acids) [4]. The plant, which was shut down in 1957, had a considerably lower production capacity than it was designed for.

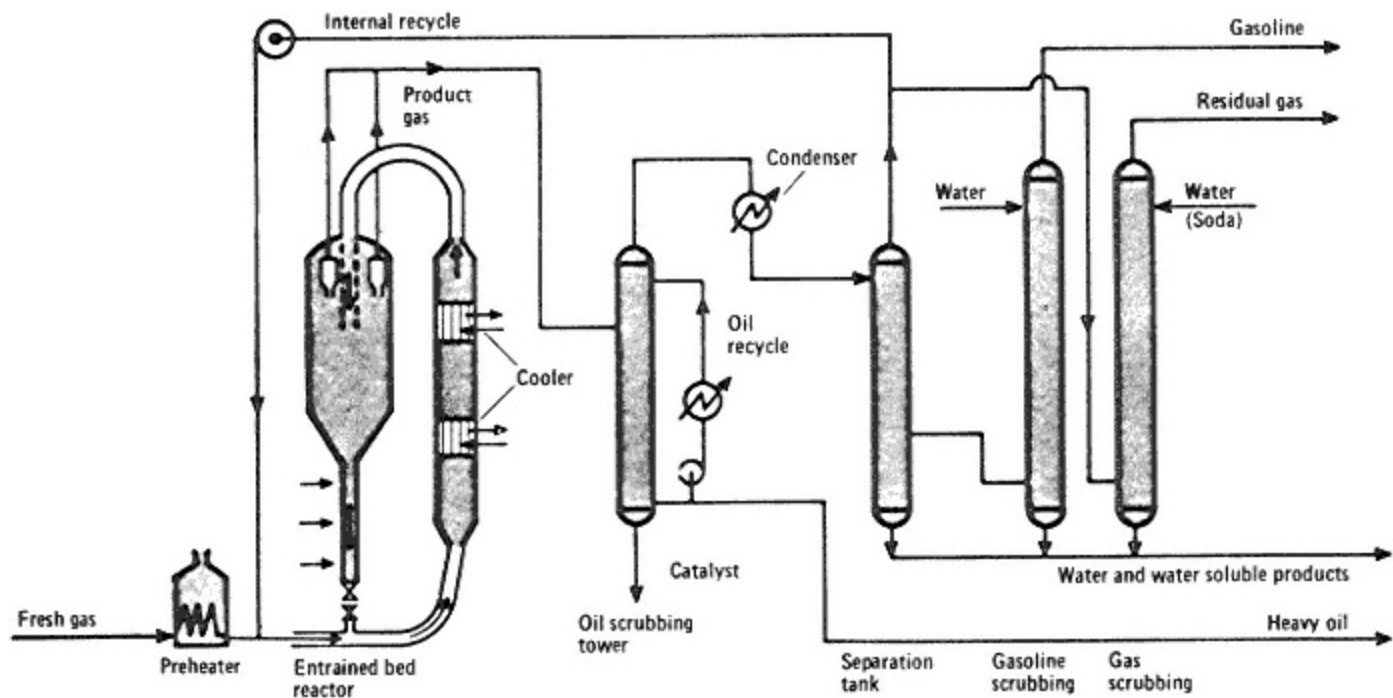


Fig. 7.
Process diagram of entrained-bed synthesis [4].
(Synthol process of Sasol)

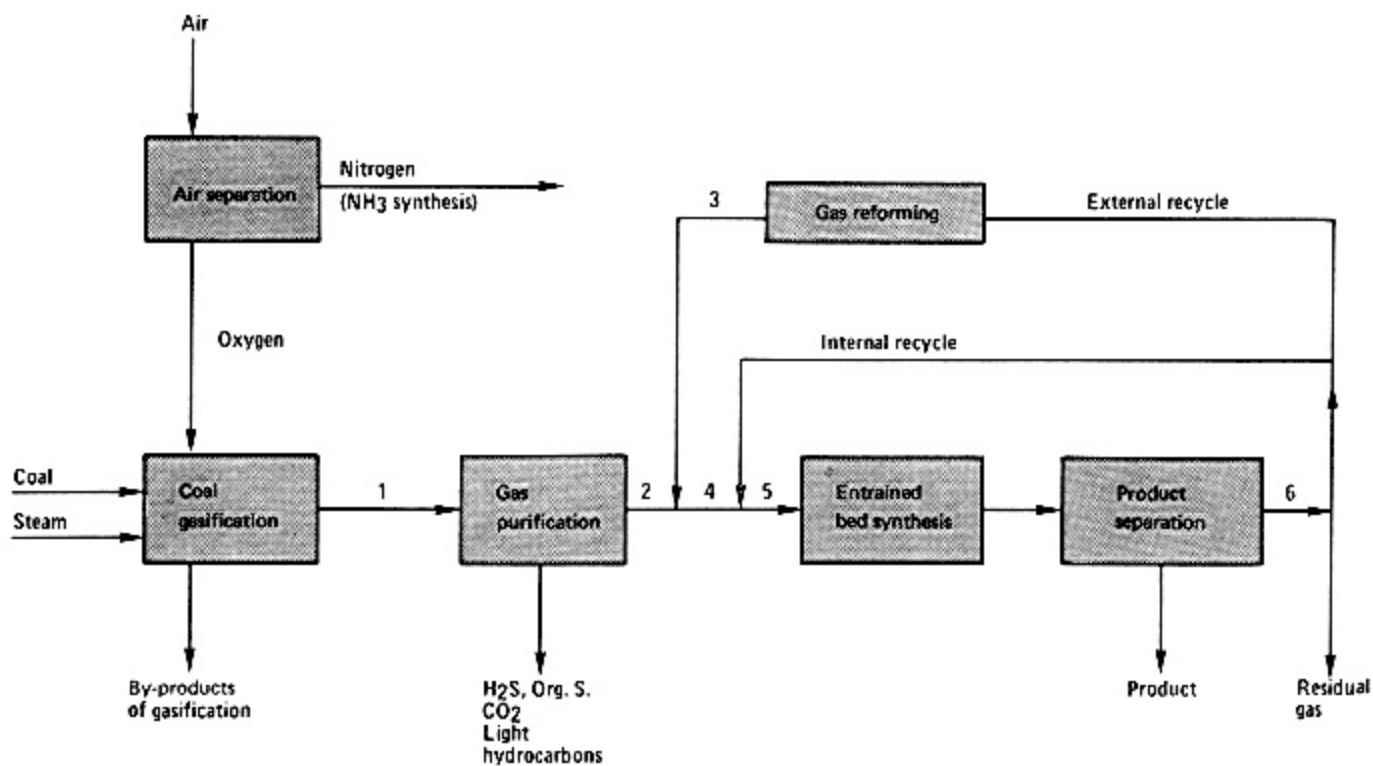


Fig. 8.

Diagram of gas flow as well as quantity and composition of gases from Sasol's entrained-bed synthesis [4, 29, 30].

No. in Fig. 8:	Raw gas	Pure gas	Product gas from reformer	Fresh gas	Total synthesis gas	Residual gas/ recycle gas (reformer feed)
	1	2	3	4	5a	6b
Gas composition (vol.%):						
CO	18	27	20	25	8.8	2
H ₂	40	59	61	60	53	50
CH ₄	9	12	4	9	29.4	38
CO ₂	31	1	12	5	3.6	3
N ₂ (Ar)	1	1	3	1	3.8	5
C _n H _m					1.4	2
H ₂ S	1					
H ₂ /CO	2.2	2.2	3	2.4	6.0	25
106 m ³ (ntp)/d	3.6	2.4	1.6	4.0	13.6	

aCalculated from 4 and 6 for H₂: CO = 6 : 1.

bResidual gas quantity amounts to 1.42×106m³ (ntp)/d; 74% is fed to the reformer, 17% to low temperature separation, and 9% as pipeline gas.

TABLE 7 Selectivity and Reaction Conditions of Entrained-Bed Synthesis [4]

Product	% of Converted Carbon
CH4	10
C2H4	4 } 10
C2H6	
C3H6	12 } 14
C3H8	
C4H8	8 } 9
C4H10	
C5C12	39
C13C18	5 } 11
C19C21	
C22C30	
C31+	
Nonacid chemicals	6
Acids	1
Reaction conditions:	
Temperature (°C)	300340
Pressure (bar)	2023
H2/CO, fresh gas	2.42.8
Total synthesis gas	56
CO + H2 conversion (%)	7785
Recycle ratio	22.4
Catalyst service life (d)	~40

The mixture of hydrogen-rich fresh and recycle gas ($H_2/CO = 3$) should move rapidly from the bottom to the top of the reactor in order to maintain a uniformly operating fluidized bed (28 bar/315°C). The product stream from the top of the reactor is separated from the catalyst by cyclones and filters. The products are obtained in a stepwise cooling process. The process diagram and an example of a product spectrum of commercial production are presented in Fig. 9 and Table 9, respectively.

3.3.3 Liquid-Phase Process

The bubble-column process with a single gas pass (without recycling) is an example of one of several liquid-phase syntheses, e.g., oil-recycling process with fixed or mobile catalyst. This synthesis is at the highest level of development. The reactor is a pressurized cylinder with a fresh gas inlet and gas distribution at the bottom, a hanging aggregate of cooling tubes (steam collecting drum), and a residual gas outlet on the top of the reactor (cf. Fig. 10).

Nonsupported catalysts doped with Cu and K_2O are suitable. The precipitated iron catalyst is finely milled to a grain size of 550 μm and suspended in products of the FT reaction (slab wax). About 200 m³ syngas (gas feed 2.5 L/g Fe) are bubbled hourly through 1 m³ of the suspension containing 515% by

TABLE 8 Summary of the Final Products Obtained on Producing Gasoline via the Entrained-Bed Process; enclosed are the by-products from the coal gasification related to 106 m³ (ntp) raw gas/h

Product	In Thousands of Tons/Year	%
Auto gasoline:		
Premium quality	615	74.2
Normal grade	263	
Diesel oil	50.6	12.2
Slab wax	39.7	
Liquid gas	53.6	
Acetaldehyde	3.1	3.4
Acetone	9.1	
Methanol	1.2	
Butanone	3.1	
Propanol	13.5	
i-Butanol	1.9	
n-Butanol	5.4	9.7
Higher alcohols	1.3	
Creosote	39.5	
Tar	15.6	
Heating oil	36.1	9.7
Aromatic solvents	3.8	
Tar acids	19.2	
Ammonium sulfate	237	
Fuel gas	24,460 m ³ (ntp)/h	
	1,175	100

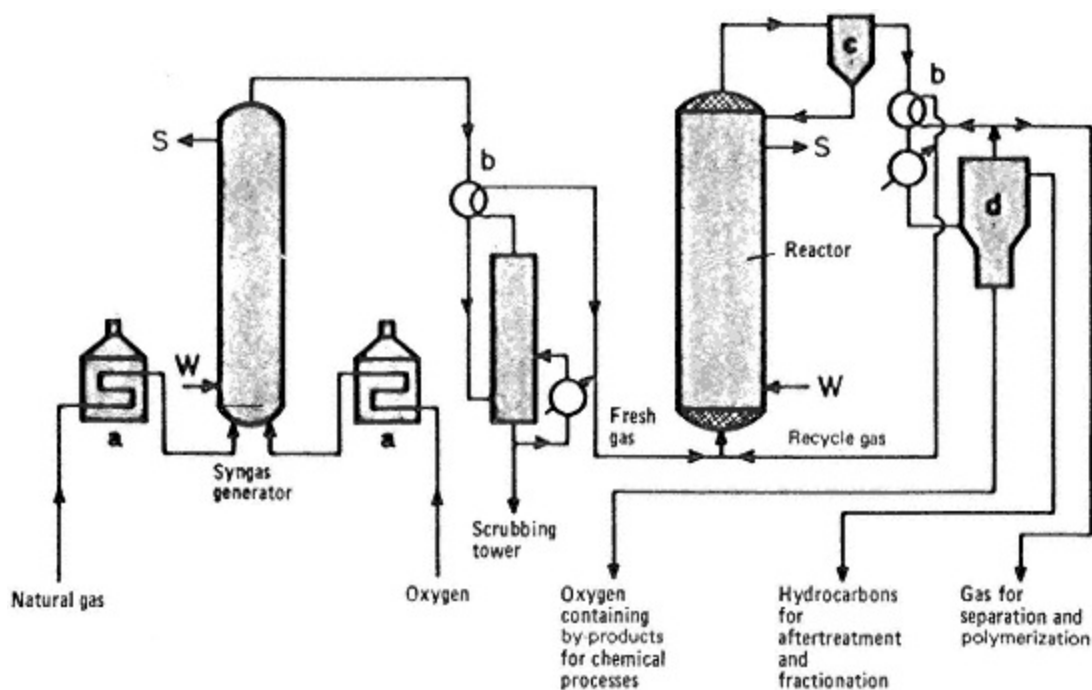


Fig. 9.
Process diagram of Hydrocol process [4].

TABLE 9 Example of the Composition of the Product Spectrum of the Hydrocol Process (commercial plant)

	% by Weight
C2	9
C3/C4	29
30-200°C boiling range	40 (85% Olefins)
200-320°C boiling range	9
>320°C boiling range	3
Water-soluble, oxygen-containing compounds	10

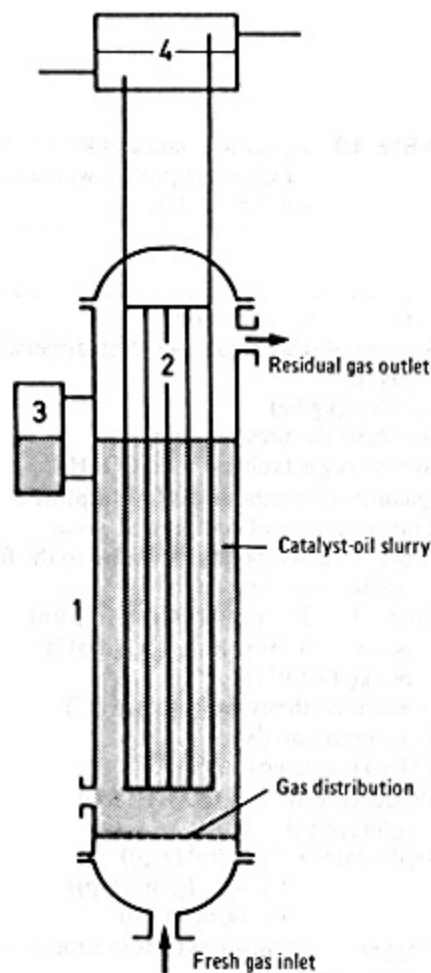


Fig. 10.
Bubble-column reactor for liquid-phase FT synthesis [17]. (1) Bubble-column reactor, (2) cooling tubes, (3) level controller, (4) steam-collecting drum.

weight of iron catalyst. The reaction gas leaving the top of the reactor is treated as shown in the diagram of the liquid-phase plant in Fig. 11.

Although the liquid-phase process has not reached industrial maturity, it has been successfully scaled up from laboratory scale (6 L suspension) to a demonstration plant (10,000 L suspension). The most difficult task was uniform gas distribution when the ratio of length to diameter of the reactors was decreased from 60:1 to 6:1. After the prevention of liquid circulation by specially constructed devices in the reactor, almost identical conversions and product spectra could be reached together with increased reactor output (cf. Table 10).

At the time when the demonstration plant was operating in 1953, the main aim was the production of high octane gasoline. As shown in Table 11, this was successfully accomplished.

Further scaling up of the liquid-phase reactor by one order of magnitude, which is expected, would lead to a daily output of around 100 tons.

TABLE 10 Operating Data and Results from Liquid-Phase Synthesis
(single-stage process with a single pass using a precipitated iron catalyst [4, 32])

	Demonstration plant	Laboratory scale
Effective reaction volume		
Volume of suspension including dispersed gas (L)	10,000	6
Catalyst (kg Fe)	880	0.4
Synthesis gas pressure (bar)	12	11
Synthesis gas (volume ratio CO : H ₂)	1.5	1.5
Quantity of synthesis gas (m ³ (ntp)/h)	2,700	1.3
Linear velocity of compressed gas at operating temperature relative to the free reactor cross section (cm/s)	9.5	3.5
Total CO + H ₂ consumed (m ³ (ntp)/h)	2,300	1.1
per m ³ reactor volume (m ³ (ntp)/h)	230	183
per kg Fe (m ³ (ntp)/h)	2.6	2.45
Average synthesis temperature (°C)	268	266
CO conversion (%)	91	90
CO + H ₂ conversion (%)	89	88
Products relative to CO + H ₂ feed (g/m ³ (ntp))		
Hydrocarbon C ₁ + (g/m ³ (ntp))	178	176
C ₁ + + C ₂ (g/m ³ (ntp))	12	11
C ₃ + (g/m ³ (ntp))	166	165
Oxygen-containing products in process water (g/m ³ (ntp))	3	2
Space/time yield of products C ₃ +, including O-products in 24 h (kg/m ³ reactor volume)	930	740

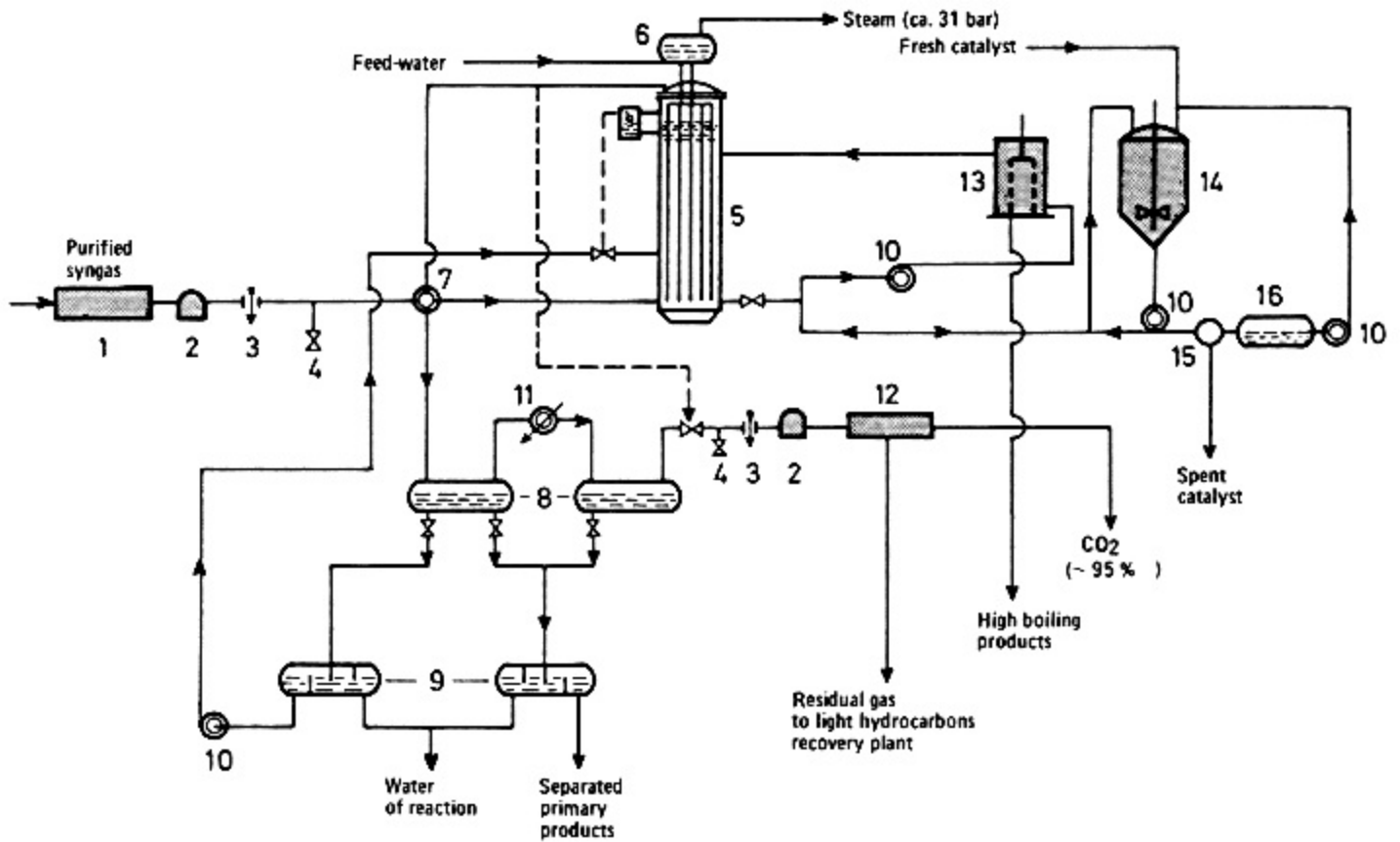


Fig. 11.

Diagram of liquid-phase plant of Rheinpreussen-Koppers (Rheinpreussen AG, Chemische Werke Moers-Meerbeck, H. Koppers GmbH)

[4, 32]. (1) Compressor, (2) gas metering, (3) valve, (4) sampling, (5) reactor, (6) steam-collecting drum, (7) heat exchanger, (8) condenser, (9) separating tank, (10) pump, (11) cooler, (12) CO₂ removal, (13) pressure filter, (14) tank for slurry catalyst, (15) centrifuge, (16) slurry oil.

TABLE 11 Composition and Properties of a Product from the Demonstration Plant (process designed to produce gasoline) [4]

	g/m ³ CO + H ₂ (ntp)	% by Weight of Total Product C1+	% Olefins	Average Molecular Weight	Specific Gravity at 20°C	Hydroxyl Number (mg KOH/g)	Acid Number (mg KOH/g)	Ester Number (mg KOH/g)
Methane + ethane	5.7	3.2	0					
Ethylene	6.3	3.6	100					
C3	40.3	22.6	7585					
C4	9.1	5.1	7080					
Fractions (°C):								
40/180	95.5	53.6	70	93.9	0.683	19.4	0.38	3.25
180/220	7.1	4.0	48	139.4	0.760	4.6	0.25	1.26
220/320	10.7	6.0	37	218.0	0.781	2.3	0.16	0.65
>320	3.3	1.9	7	300.5	0.811	0.0	0.45	1.05
Total	178.0	100.0						

TABLE 12 Variation of Molecular Weight Range of Products from Liquid-Phase Synthesis [4, 17]

Synthesis Designed to Produce Different Molecular Weight Ranges	Low	Medium	High
Yield C3+ (g/m ³ (ntp) CO + H ₂)	162	175	182
Fractions:	% share of total C3+ product		
C3 + C4	29.6	6.9	2.2
C5+ to 190°C boiling range:	63.0	40.0	7.1
190-320°C	6.2	25.7	8.3
320-450°C	1.2	18.3	33.0
>450°C		9.1	49.4

The flexibility of the liquid-phase process to different products has been briefly discussed. It is also possible to work with syngas of varying compositions (i.e., CO-rich gas to increase the olefin content). Table 12 illustrates the flexibility and versatility of the process (besides the reaction conditions, the catalyst is also very important) with regard to production in different molecular weight ranges.

Table 13 represents the composition of a product spectrum with a high content of unsaturated, short-chain hydrocarbons.

TABLE 13 Composition of a Product with a High Content of Unsaturated Low Boiling Hydrocarbons [4, 17]

Fraction	Share (%)	Olefin Content (%)
C2	4.8	83
C3 + C4	23.8	
C5	21.1	31
C6	6.6	
C7	7.3	
C8	6.9	
C9	5.0	
C10	3.0	NDa
C11C12	6.4	
C13C15	5.2	
C16C19	3.7	
>C19	4.5	
Alcohols	1.7	

aNot determined.

3.4

Assessment of Reaction Technology of Various Processes

FT syntheses are conducted in various reactors, usually under differing process and reaction conditions, using a range of catalysts. Therefore, no predictions about the most promising process technology are possible. Depending on the product spectrum i.e., whether short-chain, reactive olefins are formed as primary products, or whether wax is synthesized as a consequence of consecutive reactions an attempt must be made to correlate the important reaction parameters valid for FT synthesis based on thermodynamic calculations and reaction kinetics. Table 14 gives a survey of some characteristic data relating to different process technologies (according to Baerns [33]).

The typical features of each reactor give rise to the following conclusions.

Heat transfer is through the transfer surfaces, and the actual heat conductivity is within the catalyst. In this instance, the fixed-bed reactors exhibit disadvantages compared to other reactors. There are axial and radial temperature gradients in the reactor which may cause local superheating, resulting in a partially uncontrolled synthesis, carbon deposition, and recrystallization, combined with a favored methanation and a rapid damage of the catalyst. During large-scale operation, this disadvantage may be compensated for by increased syngas recycle.

Pressure drop as the result of syngas flow, especially at high flow rates, is least when using fixed-bed reactors. With other reactor systems, the compression energy for the gas recycle is considerably higher.

The residence time (distribution) should be as short as possible due to the production of reactive intermediates which favor consecutive reactions. This is valid for fixed-bed reactors as well as for entrained-bed units. In liquid-phase reactors the stirring effect of the ascending gas bubbles and in fluidized-bed reactors the intense mixing of catalyst and syngas favor consecutive reactions of primary products. Thus, all processes with gas recycle should use syngas free of all reactive intermediates, which may also be the desired final products. When producing long-chain saturated hydrocarbons, separation of intermediates or a low recycle ratio are normally disadvantageous for the composition of products.

As far as mechanical stress and the resulting catalyst loss is concerned, fixed-bed reactors and, to a certain extent, bubble reactors keep the catalyst loss at its lowest. On the other hand, entrained-bed processes, as well as fluidized-bed processes, are characterized by friction and catalyst losses occurring due to abrasion.

Regeneration or exchange of the catalyst during synthesis demands interruption of fixed-bed units, whereas the technologies of other processes allow this step to be conducted without interruption, i.e., via continuous purge and feed.

As shown above, the various processes differ greatly in reaction and chemical engineering methods. In every case the specific problems must be taken into account with regard to the composition of the product spectrum.

TABLE 14 Characteristic Data of Fixed-Bed, Fluidized-Bed, Entrained Fluid-Bed, and Liquid-Phase FT Reactors [33]

Characteristic Data	Reactor Type			
	Fixed-Bed	Entrained Fluid-Bed	Fluidized-Bed	Bubble Reactor
Heat transfer velocity or heat removal through transferring surfaces	Slow	Medium up to high	High	High
Actual heat conductivity within the system	Poor	Good	Good	Good
Maximum reactor diameter as limited by heat removal	~8 cma	No limitation	No limitation	No limitation
Pressure drop at high gas velocity	Small	Medium	High	Medium up to high
Residence time distribution of the gaseous phase	Narrow	Narrow	Broad	Narrow up to medium
Axial mixing of the gas	Small	Small	Large	Small up to medium
Axial mixing of the solid catalyst	None	Small	Large	Large
Catalyst concentration as volume portion of solid ($1 - \epsilon$) ^b	0.550.7	0.010.1	0.30.6	Up to a maximum of 0.6
Particle size range of the solids (mm)	15	0.010.5	0.031	0.011
Mechanical stress of the solid by shock or friction	None	Great	Great	Small
Catalyst losses	None	24% per day due to abrasion	Not recoverable discharge due to abrasion	Small
Regenerability or exchangeability of the catalyst during synthesis	Interruption of synthesis necessary	Without interruption of synthesis by continuous purge and feed		

^aA small increase seems to be possible if the heat transfer can be increased by higher gas velocities.

^b ϵ = Relative, solid free particle interspace.

4

Isolation and Work-up of the Reaction Products

As mentioned in Section 3.3.2, FT products may be obtained from different process steps of a FT plant. According to Fig. 12, these include:

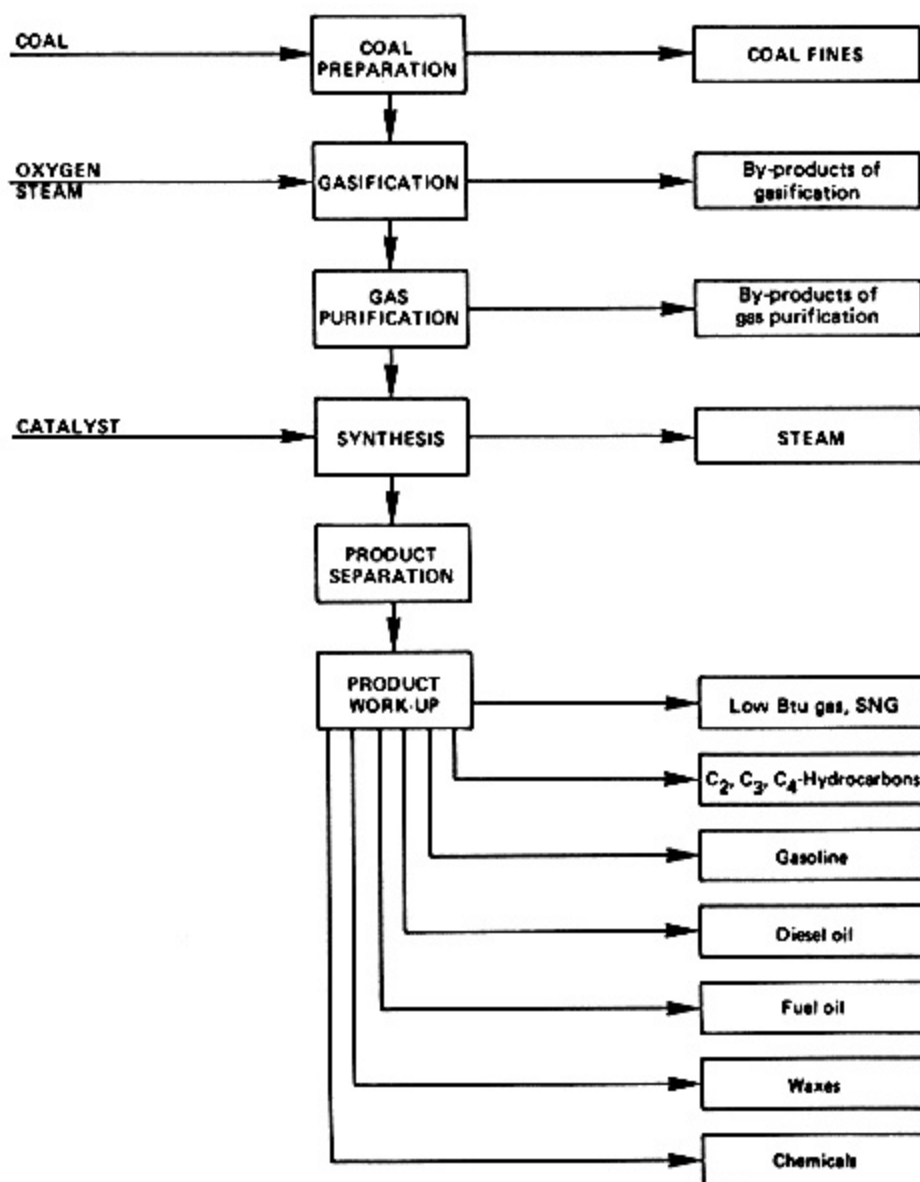


Fig. 12.
The products of FT synthesis [8, 25].

Coal fines as by-products of coal preparation

The by-products of the gasification and the gas purification (cf. Fig. 14)

Gaseous by-products of the synthesis (low Btu gas, SNG, LPG)

Gasoline and diesel oil

Fuel oil and waxes

Oxygen-containing chemicals

If a FT complex involves different process modifications, e.g., at Sasol with the ARGE and the Synthol processes, the products of both variants may be worked up jointly as shown in Fig. 13.

As can be appreciated from Fig. 13, the ARGE as well as the Synthol section of Sasol's FT plant possesses its own separation and work-up units. In the ARGE plant the first separation step is fractional condensation. At this stage, besides light oil and decanted oil, different condensates, liquid gases, and reaction water are separated. The tail gas, the aqueous phase, and the hydrocarbons of the light condensate are fed to the following separation steps: water-phase treatment, gas treatment, and hydrocarbon refining where they are treated together with the Synthol products. The following final products are recovered from light oil and decanted oil after refining, high vacuum distillation, paraffin hydrogenation, paraffin oxidation, de-oiling, paraforming (thermal cracking), and olefin separation [1, 8, 25, 3539]:

Olefins (mainly C₁₀C₁₅)

Gasoline

Diesel oil

Fuel oil

Paraffins (Sasolwaxes L)

Gatsch (slab waxes, Waksols)

Hard waxes (Sasolwaxes H)

Oxidized paraffins

More details of the work up and separation steps can be found in the literature [1, 8, 37, 39].

The gaseous products of both process units are fractionated jointly to LPG, hydrogen (low-temperature-purification for NH₃ synthesis), and/or low Btu gas/SNG. In addition, ethane/ethylene and propane/propene mixtures are isolated as important chemical feedstocks [36].

The aqueous phases from both process modifications are also treated together. After an azeotropic distillation, the following are recovered via steam stripping as chemical raw materials:

Methanol

Ethanol (Sasol brand name Ethylol)

Propanol (Propylol)
Butanol (Sabutol)
Pentanol (Pentylol)
Acetone (Saseton)
Methyl ethyl ketone (Meketon)

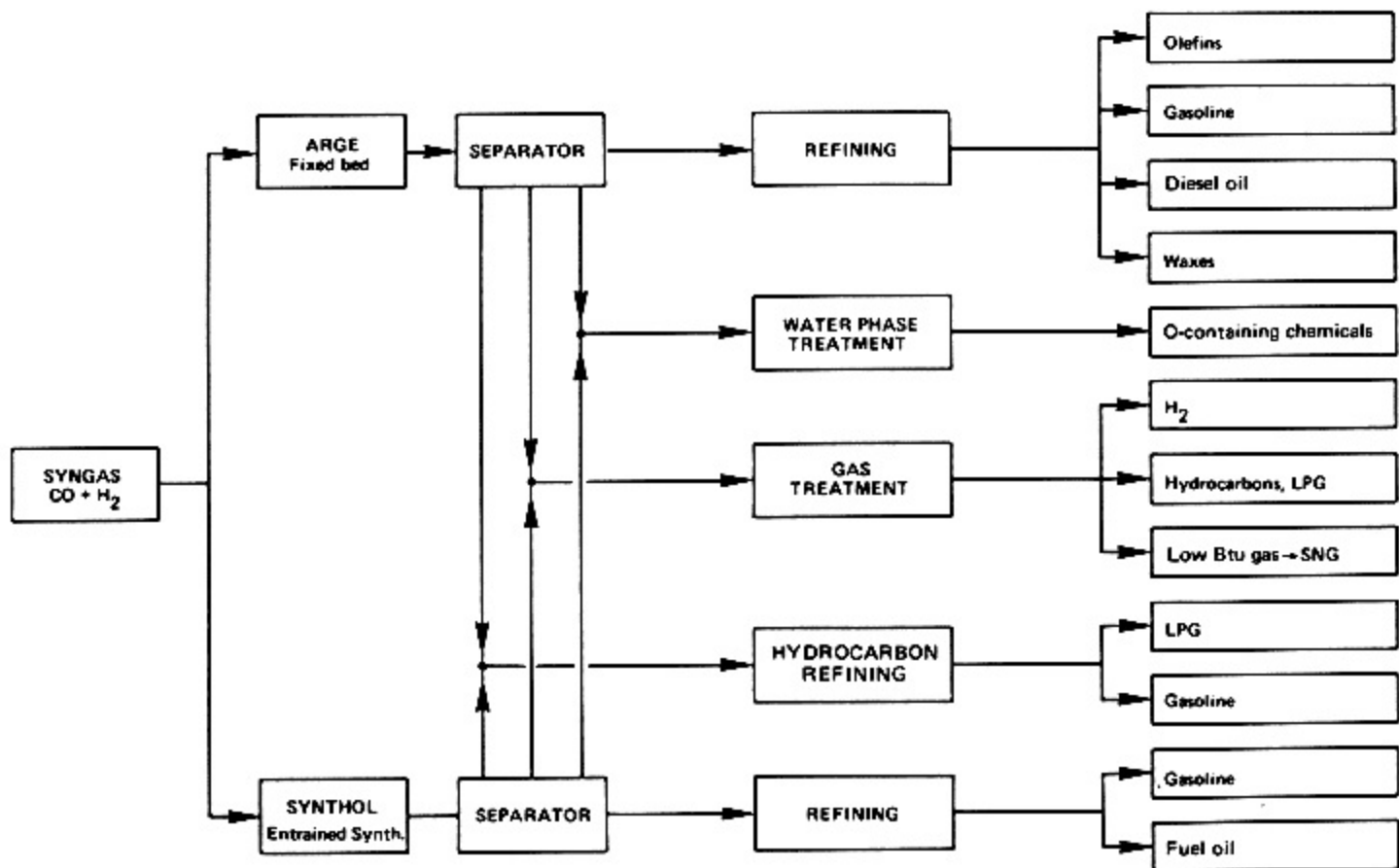


Fig. 13.
Work up of FT products [8, 34, 35].

The stream of light hydrocarbons from different units and processes possibly together with light gasoline is also worked up together ("hydrocarbon refining"). After separation of the C₂ cut, C₃/C₄ and C₅/C₅ fractions are recovered. The olefinic content is processed to polymer gasoline; the residual propane and butanes to LPG.

Refining of decanted oil includes distillation steps yielding:

- Gasoline
- Diesel oil
- Fuel oil
- Residual waxes (Waksol K)

In addition, a large variety of working-up processes are known [4048].

Besides these products of the actual FT synthesis, the by-products of gasification and gas purification are also recovered as shown in Fig. 14.

According to Fig. 14, the gas liquors from the Lurgi gasifiers are separated (after cooling) in a gas liquor separation step. An oil and tar fraction (to tar distillation) and an effluent stream (to Phenosolvan washing) are obtained. The off-gas of the Rectisol purification, as well as the acid gas of the Phenosolvan scrubbing, passes a Stretford step for sulfur recovery.

Besides the main products of FT synthesis, the following substances are recovered as by-products of gas generation and purification:

- Creosotes
- Pitch
- Residue oil
- Ammonia (ammonium sulfate)
- Phenols
- Sulfur
- Naphtha

Thus the total output of a FT plant includes aromatics besides the main product aliphatic compounds.

An example of the quantitative relationship between feedstock and products of a modern FT unit is presented in Table 15. These data are based on results from the Sasol II plant.

5

Economical Aspects and Possibilities for Further Developing FT Synthesis

Until now, all industrial applications of the "notoriously unselective FT synthesis" [34] have been largely based on establishing a native supply of raw materials in the producing countries. Germany and the Republic of South

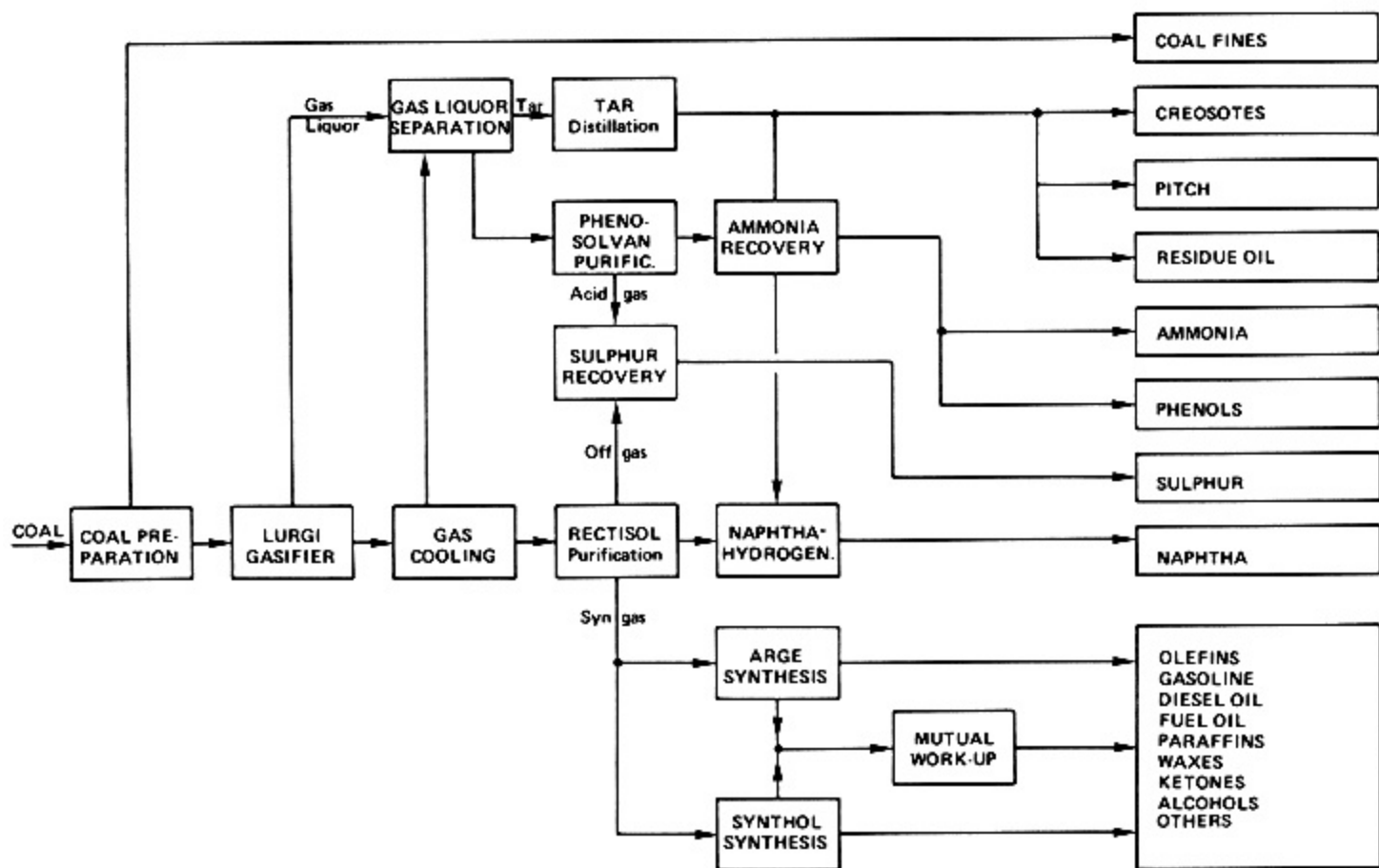


Fig. 14.

Flow diagram of coal gasification, syntheses, and product purification of the Sasol complex [3638].

TABLE 15 Sasol II Feed and Products [36] (data in tons per year, cf. Table 8)

Input	Output
11,300,000 t coal	100,000 t ammonia
	90,000 t sulfur
	240,000 t phenols
	creosotes
	pitch
	resid oils
	1,500,000 t LPG
	gasoline
	diesel oil
	fuel oil
	chemicals

Africa are obvious examples, as well as the briefly operated licensed units in Japan, Manchuria, and Italy.

FT plants in France (Société Kuhlmann with license of Ruhrchemie/Lurgi), in the United States (Hydrocol fluidized-bed unit) and in Germany after World War II had to capitulate in the mid-fifties in the face of cheap mineral oil and its ready processing. The availability of both motor fuels and chemical feedstocks from inexpensive, easy-to-handle mineral oil made FT plants uneconomic even at plant locations with cheap sources of coal. Consequently, Sasol has been the sole producer of FT products for over 25 years.

However, this situation will change. With the background of the oil supply crises and the vulnerability of the industrialized nations against "blackmailing" in the form of their oil delivery being stopped, coal will gain more and more importance as an alternative source of fossil carbon for energy requirements and chemical feedstocks. The reason for this is that coal is available for a much longer period than oil and is more uniformly distributed throughout the world. Thus, work is being conducted internationally on improving coal processing and coal refining.

FT synthesis has good prospects of becoming a standard procedure for coal refining in the future. The following reasons are particularly valid.

1. As a syngas process, FT units may be connected to any syngas infrastructure and thus be supplied with CO/H₂ mixtures of different origins (heavy oil, coal, wood, carbon-containing waste, etc.). All improvements during development of the coal gasification processes of the "second generation" may be fully implemented.
2. The combination of a coal hydrogenation and a subsequent FT unit is of special value. The high boiling residues of coal hydrogenation may be gasified by those coal gasification processes of the "second generation" which are able to handle liquid feedstocks and which allow a gasification which eliminates the environmental pollution of previous times. The resulting syngas may feed subsequent FT units. The combination of the product

stream of both plants results in an ideal product mix for high

standard gasoline and diesel oil. Besides motor fuels, such a plant combination also yields chemical feedstocks in considerable amounts.

3. The FT process may be controlled between certain limits even when the reaction parameters are varied. Catalyst variation presents great potential for influencing the selectivity of the process. Today, work concentrating on shifting the FT product spectrum toward lower olefins is in the foreground ("modified FT synthesis"). According to the first results, future FT plants may be used for the production of chemical feedstocks rather than for the synthesis of motor fuels [19, 4954].

Thus, FT synthesis has to be regarded as being included in a whole complex of syngas reactions which make available a large variety of chemicals, besides being the classical route to motor fuels (cf. Fig. 15 [22])

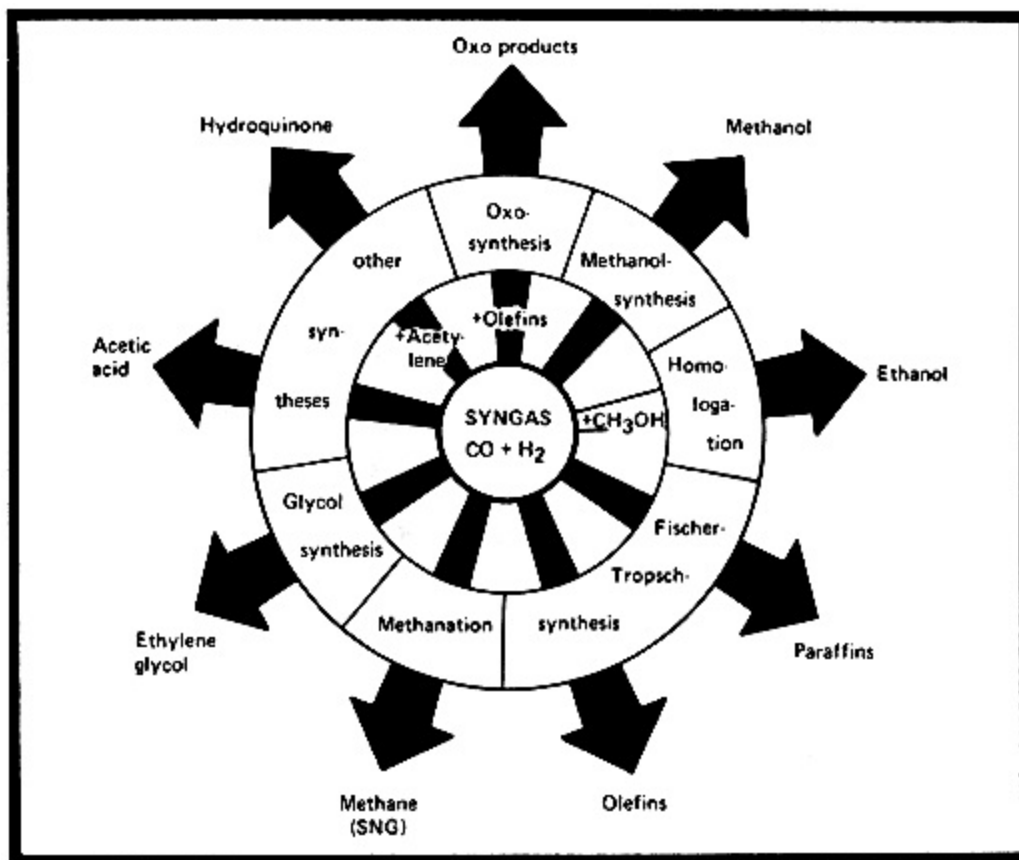


Fig. 15.
Syngas chemistry for chemical feedstocks [22].

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Hydrogenation Catalysts

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Hydrotreatment originally included hydrodesulfurization, hydrodenitrification, and some hydrogenation. Gradually the hydrogenation of unsaturated hydrocarbons became specific with original processes and catalysts. Interest in these specific processes began during World War II (hydrofining of alkylation feedstocks) but the kick-off was in the sixties, with the booming growth of naphtha cracking for olefins. These nonselective thermal processes produced a full range of unsaturated hydrocarbons. Hydrotreatment (as hydro-

TABLE 1 Various Hydrogenation Processes

Source	Cut	Impurity	Valuable Product	Use
Steam cracking	C2's	Acetylene	Ethylene	Petrochemistry
	C3's	Methylacetylene/ propadiene	Propylene	Petrochemistry
	C4's	Vinylacetylene	Butadiene	Petrochemistry
	C4's	Butadiene	Butenes	Petrochemistry
	C4's	Butadiene	1-Butene	Petrochemistry
	Pyrolysis	Dienes	Olefins	Gasoline pool
	Naphtha		Aromatics	
Catalytic cracking	C3's	Methylacetylene/ propadiene	Propylene	Gasoline pool or petrochemistry (Dimersol) ^a
	C3's, C4's	Methylacetylene/ propadiene	Butenes	Gasoline pool or petrochemistry (Dimersol) ^a
		Butadiene	Propylene	(Alkylation or oligomerization)
Fluid coking	C3's C4's	Butadiene	Propylene	Petrochemistry or gasoline pool
	Pyrolysis	Dienes	Olefins	Gasoline pool
	Naphtha			
Hydrodealkylation B.T.X.		Dienes	Benzene	Petrochemistry
		Olefins		
		Thiophene		

^aDimersol = Institut Français du Pétrole olefins dimerization process with soluble catalyst.

fining) was used for the removal of impurities by selective hydrogenation, e.g., selective hydrogenation of acetylene in the ethylene-rich cut.

The specificity of the downstream petrochemical uses require very stringent quality for the products, and consequently very efficient catalysts and purifications. The increased prices of crudes favor the diversification of sources and other cracking processes than steam cracking supply feedstocks for petrochemistry (Table 1). This evolution brings about new requirements for the hydrogenation catalysts and motivates constant improvement.

Hydrogenation Catalysts

FSSabatier (1902) first demonstrated the ability of metal catalysts to activate the hydrogenation of double and triple bonds in the vapor phase at atmospheric pressure. At the same time, Ipatieff performed liquid-phase hydrogenation under high H₂ pressure. Since these discoveries, many industrial applications have been developed.

For the selective hydrogenation of acetylenics and diolefins, the first generation catalysts were sulfided catalysts such as nickel sulfide [1] or nickel tungsten sulfide [2].

Copper-based catalysts were also used for selective vapor-phase hydrogenations [3, 4].

The first-generation catalysts, because of their low activity, were used at rather high temperatures. For this reason some polymerization occurred, resulting in catalyst plugging, activity and selectivity decrease, and very short cycle lengths.

A second generation of catalysts was palladium based. Fundamental research [5] has proven that, among the metals of Group VIII, palladium is the most active and selective metal for the hydrogenation of acetylenics and diolefins to the corresponding olefins. Several new processes were based on this new type of catalyst such as those described in the references [610].

The world petroleum crisis has increased the demand for more selective processes to save energy and raw materials. In the case of hydrogenation, the demand for more efficient plants cannot be satisfied with conventional catalysts.

Even if palladium is the most suitable metal for selective hydrogenations, its use has several disadvantages.

Activity

Palladium is the best metal for acetylenic and diolefin hydrogenation, though its activity is still too low in some specific circumstances. For example, with feeds containing sulfur components such as mercaptans or sulfides, palladium catalysts, while not poisoned, are so strongly inhibited that operating the plant is not valid with such a drastically reduced conversion level.

Selectivity

The selectivity of hydrogenation is restricted by several competitive reactions:

Saturation: An attempt is made to obtain highest yield of the intermediate unsaturated component while avoiding as much as possible the complete saturation of the hydrocarbon. For this purpose, palladium is generally very satisfactory, but can still be improved upon.

Olefin double bond shift: This special case of selectivity is very important for the recovery of 1-butene from C₄ olefin cuts containing residual butadiene. For this application, palladium is not the right catalyst. As a matter of fact, its high activity for double bond shift is used for the production of 2-butenes from 1-butene, which is often of interest because 2-butenes are preferred for several butenes uses (hydration or dehydrogenation, alkylation).

Oligomerization: Another expected improvement is a decrease of the formation of oligomers (low molecular weight polymers with various structures). On palladium catalysts, oligomerization takes place during any hydrogenation of highly unsaturated components (C₆ and C₉ olefins during hydrofining or propylene-rich cuts, green oils during

C2 cut hydrofining, etc.).

Stability

Palladium catalysts withstand well the usual organic impurities which act solely as activity moderators; nevertheless, they are poisoned by a few of them, e.g., COS and H₂S at low temperature. The oligomerization activity of palladium results in another type of unstability. The oligomers foul the catalyst and the activity decreases with time, therefore the cycle length is limited.

As a consequence of these imperfections of the conventional palladium-based catalysts, the existing hydrogenation processes, as well as any process, have operating problems.

1. In selective hydrogenation of acetylene in ethylene-rich cuts, oligomerization results in a reduction of ethylene recovery and in limited cycle time.
2. In selective hydrogenation of methylacetylene and propadiene in propylene-rich cuts in the vapor phase, oligomerization causes the same problems as above. In liquid-phase operation, these two disadvantages (olefin losses and short cycle time) are almost eliminated but some improvement in propylene gain (hydrogenation of C₃H₄ to C₃H₆) are still expected. Moreover, when the feed to the hydrogenation unit contains FCC C₃ imports, fast catalyst deactivation occurs in most cases since cat cracking fractions contain specific contaminants, e.g., arsine and carbonyl sulfide. Recovery of propylene from refinery diluted streams is very interesting today, and there is therefore a strong economic incentive to tentatively overcome this instability.
3. In selective hydrogenation of vinylacetylene in butadiene-rich cuts when seeking 100% butadiene recovery in the solvent extraction operation, there are two operating troubles: Butadiene losses even at moderate conversion of acetylenics, and short catalyst life due to palladium losses.
4. Selective hydrogenation of butadiene in 1-butene-rich cuts is important because of the high demand for polymer-grade 1-butene as a comonomer for linear low density polyethylene. The various processing schemes always involve a hydrogenation step in order to eliminate butadiene. Hydrogenation of 1-butene is easily limited with conventional palladium catalysts, but the same catalysts promote isomerization of 1-butene to 2-butenes. The resulting 1-butene losses may be high enough (above 10%) to jeopardize the economics of 1-butene recovery.

To meet these many challenges, Procatalyse and Institut Français du Pétrole (I.F.P.) have produced new improved bimetallic catalysts which comprise palladium and a second metal deposited on a convenient support. On the basis of new concepts developed in the field of heterogeneous and homogeneous catalysts, we have been able to select the second metal efficiently.

One concept is the theory of hard and soft acids and bases developed by Pearson [11]. The Group VIII metals have an acidic character depending on their location in the periodic

table. Such acidic properties of the metal result in reactions which are generally promoted by acid catalysts, e.g., silica-

alumina. This is the case of oligomerization and isomerization of olefins (double bond shift).

Another concept comes from organometallic chemistry and homogeneous catalysis. The lability of ligands governs the stability, reactivity, and catalytic properties of the organometallic compounds. From the very abundant results and knowledge accumulated on homogeneous catalytic hydrogenation, it can be deduced that such reagents as alkynes, diolefins, and olefins, can also act as ligands. Recent results obtained in our labs [1214] have shown that this idea can be usefully applied in heterogeneous catalysis.

Alkynes and diolefins are very strongly bound to palladium. This effect results in self-inhibition of the catalyst. It is particularly the case for alkynes and specifically for vinylacetylene. The too-strong complexation of this hydrocarbon even results in palladium dissolution from the catalyst support. Such a formation of a stable organometallic compound with acetylenics and diolefins is known to occur in coordination chemistry [15].

Furthermore, the stability of the organo compound can be controlled by choosing the appropriate ligand. As a very important result, we have found [16] that it is possible to make use of this last concept for supported metals like palladium on alumina. Figure 1 illustrates such a possibility. The hydrogenation of 1-butyne and subsequent 1-butene traced by hydrogen uptake as a function of time is represented. Curve A presents the hydrogenation in 1-butyne without any additive. The hydrogenation rate of 1-butyne is rather low until its complete hydrogenation (100% of stoichiometry for H_2). The hydrogenation of 1-butene which follows is, on the other hand, quicker. In Curve B with piperidine added, we can observe that the 1-butyne hydrogenation rate is much higher and that 1-butene hydrogenation is strongly inhibited. This increase of both activity and selectivity is interpreted as a decrease of the too-

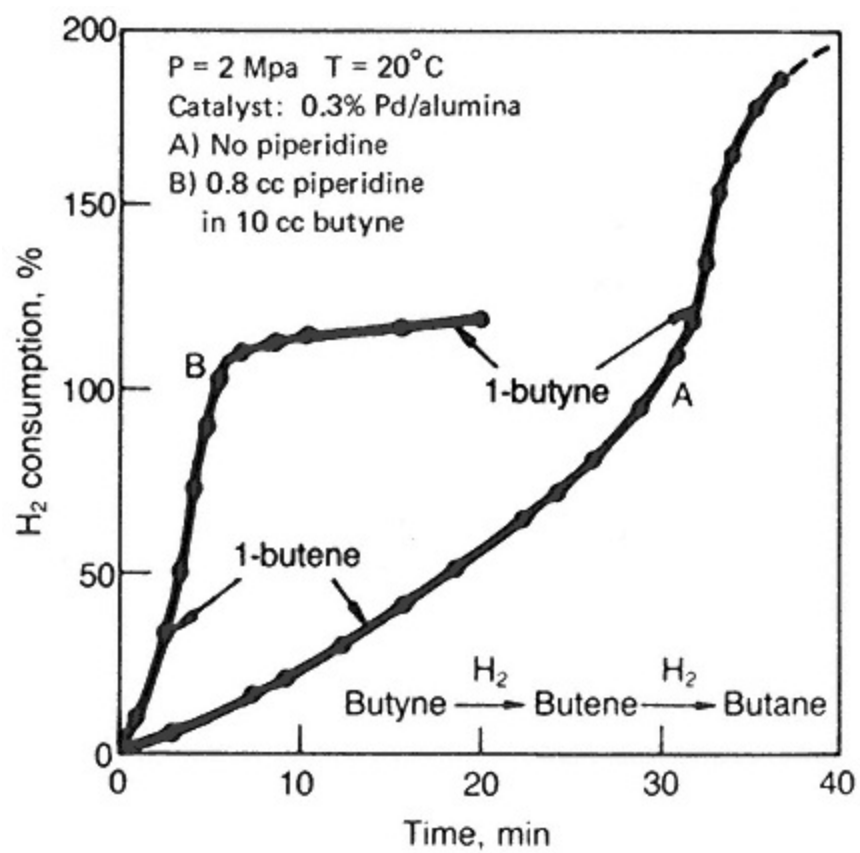


Fig. 1.
Influence of piperidine on hydrogenation of 1-butyne and 1-butene.

strong alkynemetal bond, induced by an electrodonating compound like piperidine which acts as a ligand.

This last result is very interesting and useful but it cannot be used as such for improving industrial catalysts. For example, addition of nitrogen compounds to petrochemical feedstocks can be detrimental for further uses in chemistry and thus is incompatible with industrial practice. Thus it is necessary to improve the palladium by direct addition on the metal of an element which acts similarly to piperidine but remains on the solid catalyst. Such elements can be found in the periodic table, e.g., metals of Group Ib.

However, the selection of the proper promotor is, by far, insufficient to obtain a good industrial catalyst. It is absolutely necessary to obtain and to control the intimate contact of both metals. This is the reason why we have developed new methods using, at a given stage of the preparation, a specific interaction between the two metals to be deposited. This is briefly summarized below.

Catalyst Preparation

Bimetallic catalysts in hydrogenation are not new [17], but industrial applications have been restricted to the base metals, e.g., nickel plus copper, molybdenum, or tungsten. The multimetallic catalysts with precious metals have been synthesized in laboratories but have very few, if any, industrial hydrogenation applications. The most obvious reason for this lack of application may be the metal loadings of these laboratory catalysts 1 to 10 wt.%. Commercial industrial metallic catalysts with precious metals have generally less than 0.3 wt.% loading.

In fact, at these low levels it is almost impossible to obtain a controlled supported bimetallic catalyst by using simple methods such as co-impregnation. With such methods the major parts of both metals are located separately on the carrier and do not interact.

Recent advances in the field of fine inorganic chemistry and organometallic compounds allow new preparation methods which improve greatly the synthetic route to new, well-dispersed bimetallic species. Several possible methods [1824] are listed below:

Decomposition of an organometallic compound by a first metal preliminarily deposited on the carrier

Reduction of an organometallic compound by a first metal already deposited and reduced

Impregnation of the support with bimetallic clusters

Coprecipitation of mixed oxides in the carrier pores and subsequent reduction

Deposit of a second metal on a first one introduced in the oxide state as support and using the S.M.S.I. (strong metal support interaction)

Vapor condensation of the two metals on the carrier, either in one step or in two steps

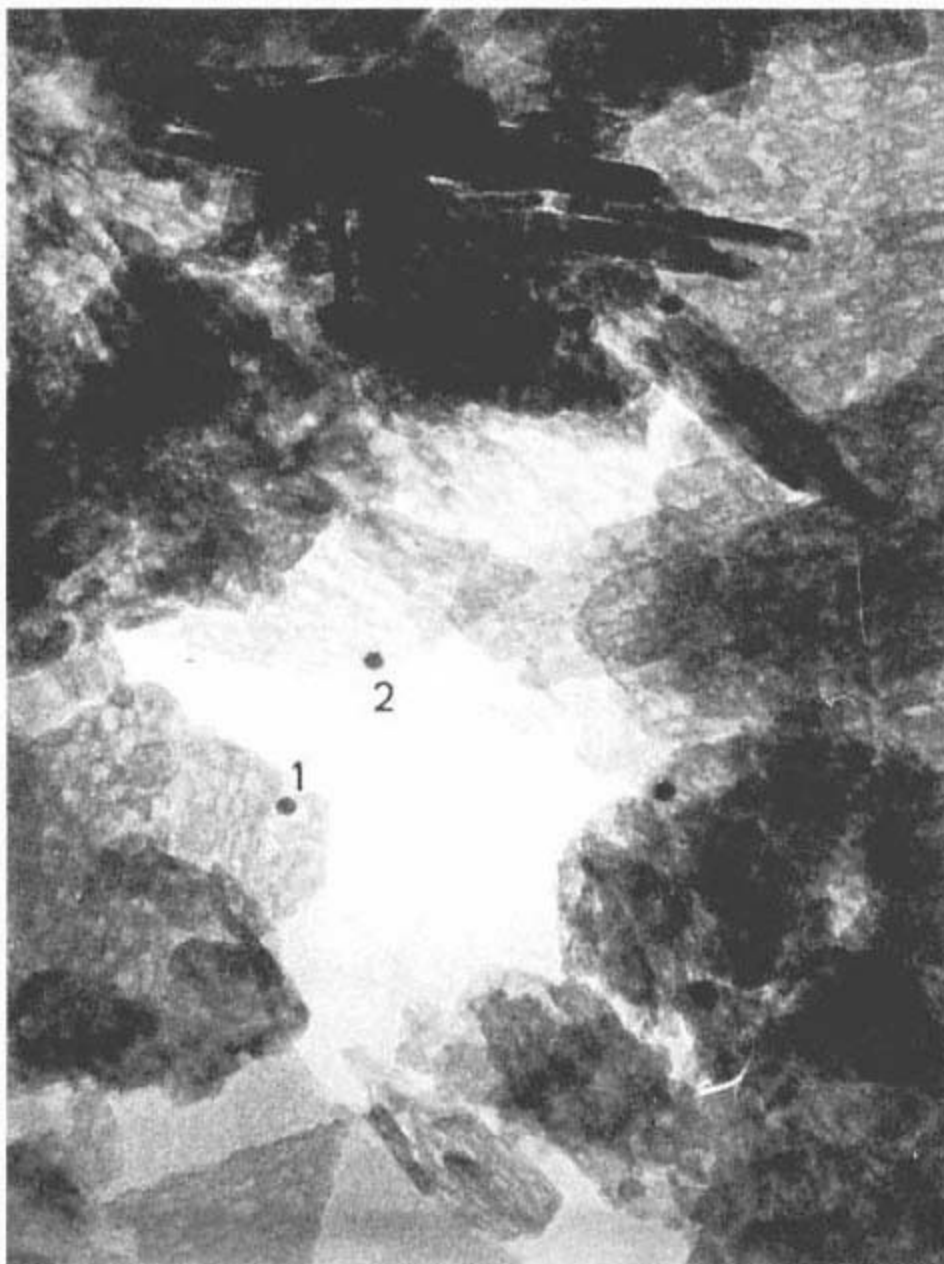


Fig. 2.
Electron micrograph of a platinum-gold catalyst.

All these methods are potentially attractive and the best selection must be made. First of all, a suitable carrier must be chosen in such a way that it allows appropriate interaction between both metals. In the contrary case, the result would be two separate metals. Second, the bimetallic species obtained must be maintained, and again, a too-strong interaction between carrier and one of the metals would favor detrimental segregation during the life of the catalyst. Last but not least, the selected method must be industrially and economically feasible.

Even with these few guidelines it is not obvious which method is the most adequate and how to discriminate the best from the others.

Until recently, improvements in bimetallic supported catalysts were only made by lengthy trial-and-error research. This was because it was nearly impossible to analyze the metal particles deposited on the support. Thus the composition of these particles was unknown, and the improvement of palladium by adding a second metal was more a question of chance than of expertise. The recent development of modern methods of microscopic characterization and analysis of metal surfaces has provided new facilities for controlling bimetallic catalysts.

Figures 2 and 3 show such an example of particle analysis by using the STEM (scanning transmission electron microscopy) technique. The apparatus used is a vacuum generator HBS STEM, equipped with a kevox detector for x-ray emission microanalysis. Figure 2 is an electron micrograph showing several metallic particles. Figure 3 presents the microanalysis of two of them that are both bimetallic.

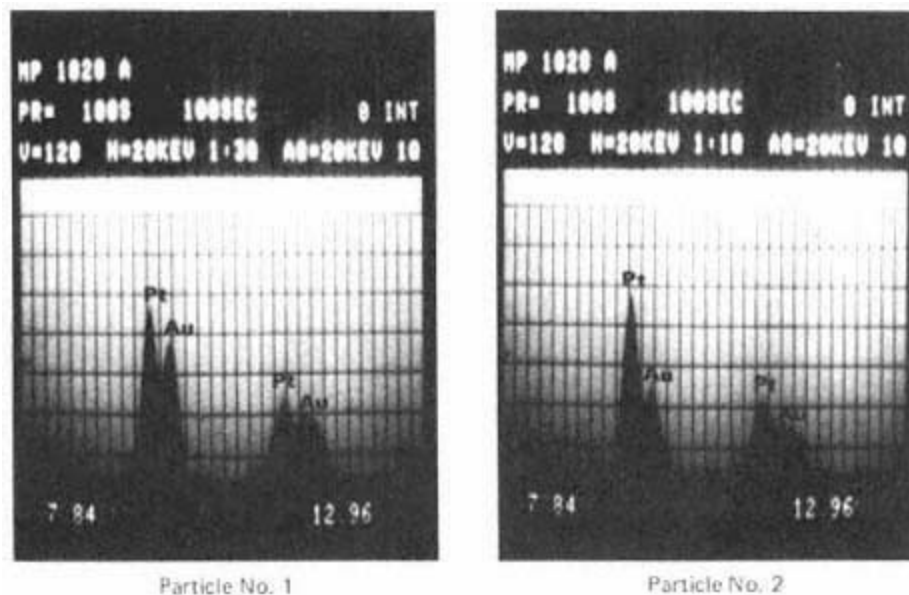


Fig. 3.
X-ray emission microanalysis of platinum-gold particles.

Steam Cracking C2 Cut

The selective removal of acetylene in an ethylene-rich cut is mandatory to meet the ethylene specifications, and selective hydrogenation is usually used. This hydrotreatment is done with palladium catalysts in two or three reactors in series at 25 bar and between 40 and 110°C.

Acetylene Polymerization

The existing process meets the ethylene specifications but at the expense of yield. The hydrogenation of acetylene is not 100% selective and some ethylene is hydrogenated. Moreover, the catalyst is rapidly plugged by polymers, which results in frequent regeneration.

Mechanistic studies [2528] of this hydrogenation have large discrepancies. The most established reaction scheme, however, considers the oligomerization as a parallel reaction to acetylene hydrogenation. A strict relation between the hydrogenation and the polymerization has been shown (Fig. 4).

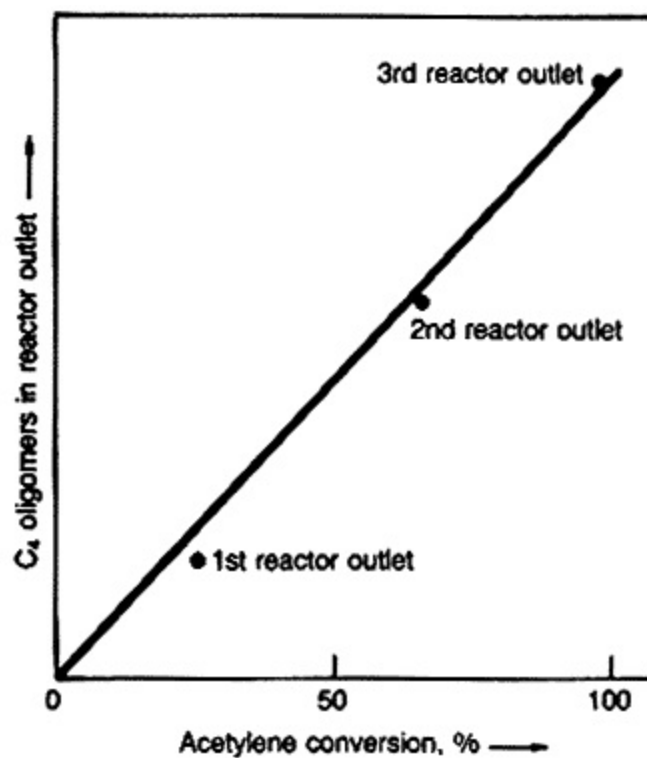


Fig. 4.

Relation between C₄ oligomers content and acetylene conversion in industrial reactors.

TABLE 2 Composition of the
C8+ Oligomers

	wt. %
C8	45
C10	23
C12	12
C14	6
C16	3
C18	3
C20	2.4
C22	1.9
C24	1.4
C26	1.3

The formation of C₄ oligomers and the hydrogenation of acetylene are proportional. This result is in accordance with work by others [29]. In addition, it has been found that no polymerization occurs without hydrogen injection [30]. More precisely, the oligomers seem to be formed by condensation of acetylene on itself. McGown et al. [31] highlighted this fact with the following observation. The oligomers formed during the hydrogenation of a mixture of propylene and acetylene do not contain C₅ compounds, which excludes the participation of the olefin.

Table 2 shows the composition of the C₈+ oligomers (green oil) formed in C₂ hydrogenation performed in pilot plant. The periodicity (C₂)_n is clear.

New Catalyst

All these data clearly indicate that the polymerization reaction is intrinsically bound to the hydrogenation activity of the palladium. It is therefore illusory to hope for a drastic change of these figures by just adjusting the operating conditions. The only way to obtain better yields and to improve the stability of the catalysts is through the modification of palladium properties.

Careful examination of its metallic properties and of the interactions developed by alloying with other metals allowed us to select the best promoter. Figure 5 reports the ethylene yields and acetylene conversions for several quantities of promoter added to the palladium. The feedstock is a mixture of ethylene (98.9 wt.%) and acetylene (1.1 wt.%).

It is clear that an optimum ratio of promoter over palladium content exists. This optimum composition has been selected for the new catalyst (LT 279). This promoted catalyst is superior to the conventional one both for ethylene yield and acetylene hydrogenation activity. Figure 6 reports the results obtained in an accelerated aging test. Both catalysts (conventional palladium and promoted palladium) have been used during 200 h in similar operating conditions (GHSV = 2500, 25 bar, 60°C) in the hydrogenation of a C₂ cut with 2% acetylene content. These conditions (high space velocity and

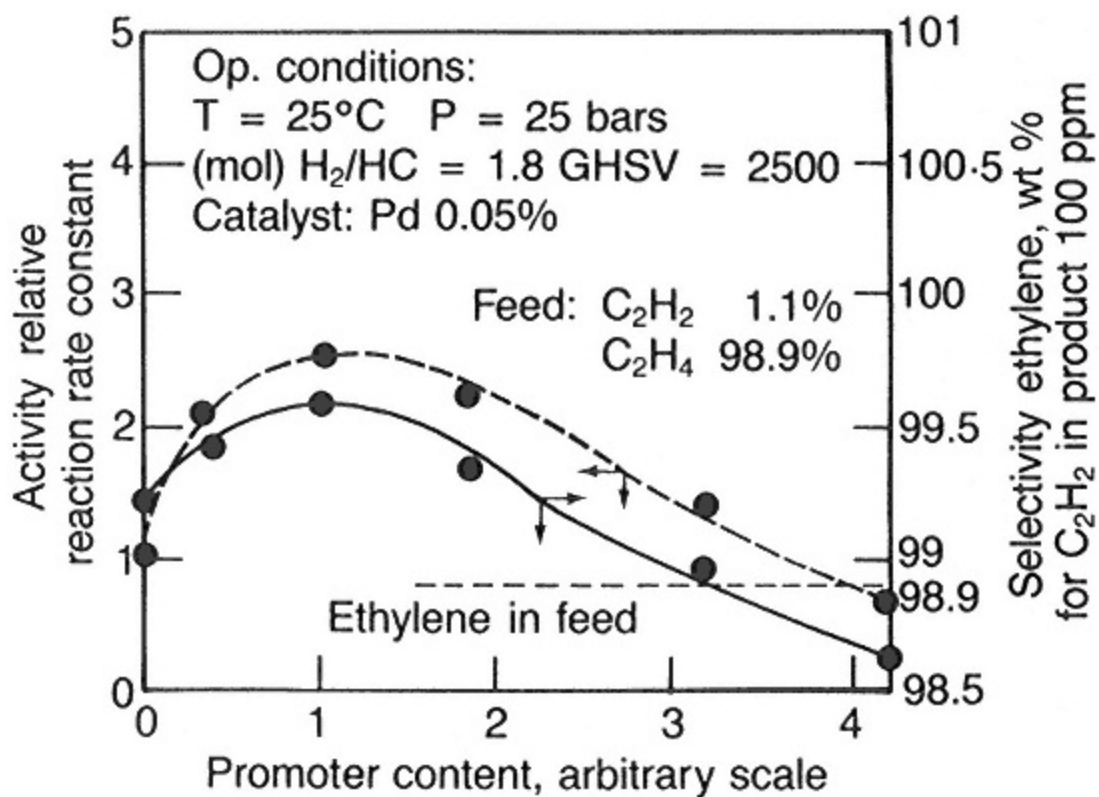


Fig. 5.

Influence of promoter content on the activity and selectivity of acetylene selective hydrogenation catalyst.

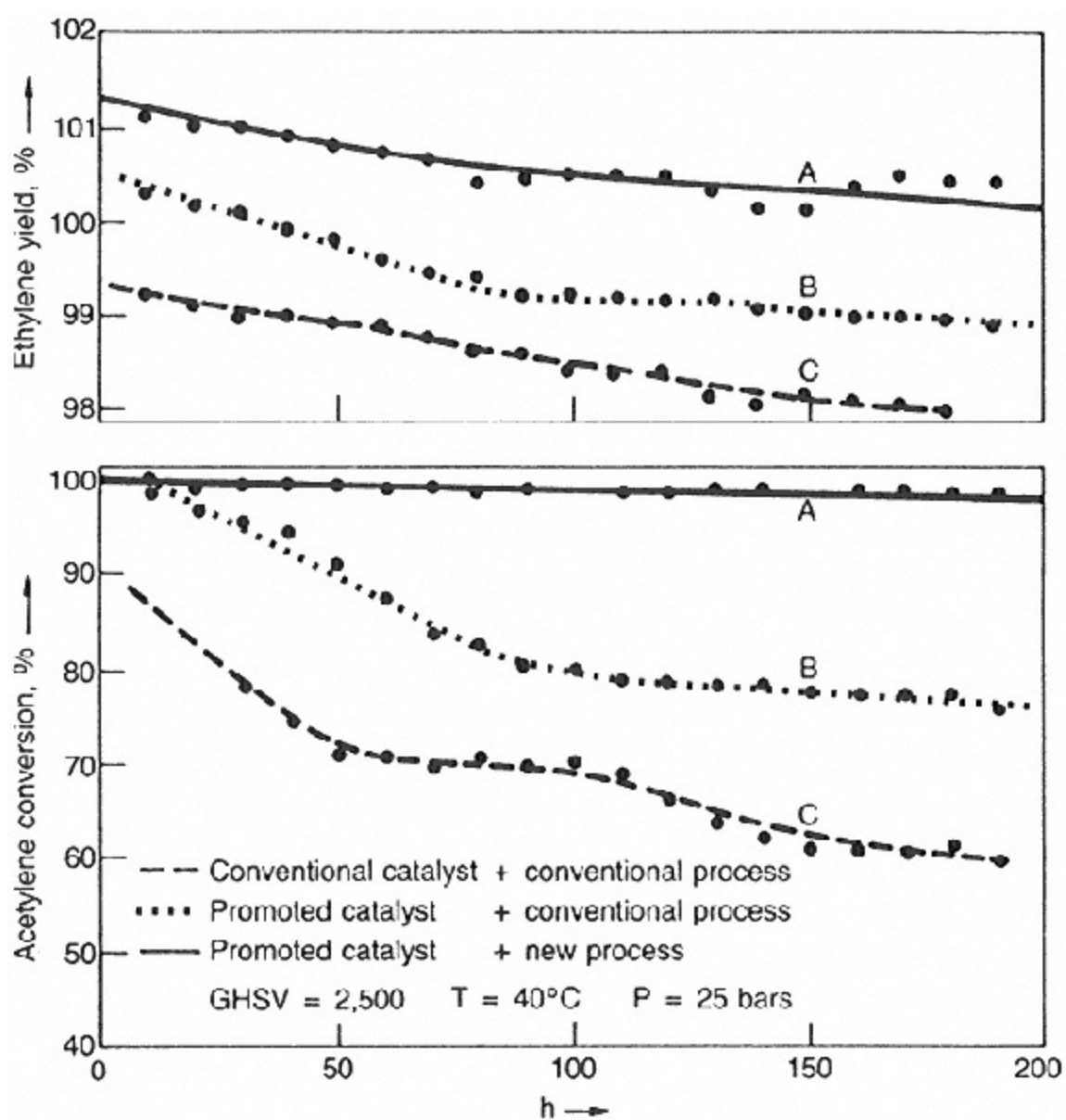


Fig. 6.
Acetylene conversion and ethylene yield obtained with different catalytic systems.

very high acetylene content) are very detrimental to the process, and a continuous deactivation is generally experienced during such an operation. The deactivation of the catalyst is always accompanied by a decrease of the ethylene yield. Curves A and B show that the promoted catalyst remains superior for both acetylene conversion and ethylene yield throughout the test.

New Process

Nevertheless, the stability in such conditions is not yet completely satisfactory, and definite progress has been obtained by the combination of this promoted catalyst and a new process (Curve A). In fact, our industrial experience with the C3 cut hydrogenation has demonstrated the advantages of the liquid phase over the gaseous one. With the liquid phase we experienced catalyst cycles of more than 2 years, with space velocities much higher than for gaseous phase units.

This superiority of the liquid phase is unanimously attributed to the action of the liquid that washes out the green oils formed. However, the liquid state of a C2 cut cannot be obtained in practical conditions of temperature and pressure compatible with hydrogenation. The solution adopted by I.F.P. has been a hydrogenation solvent. This solvent is separated from the hydrogenated C2 cut in a flash drum and recirculated to the reactor where it is recontacted with the fresh feed (Fig. 7). Such a process has been tested extensively in a pilot plant and has these typical features:

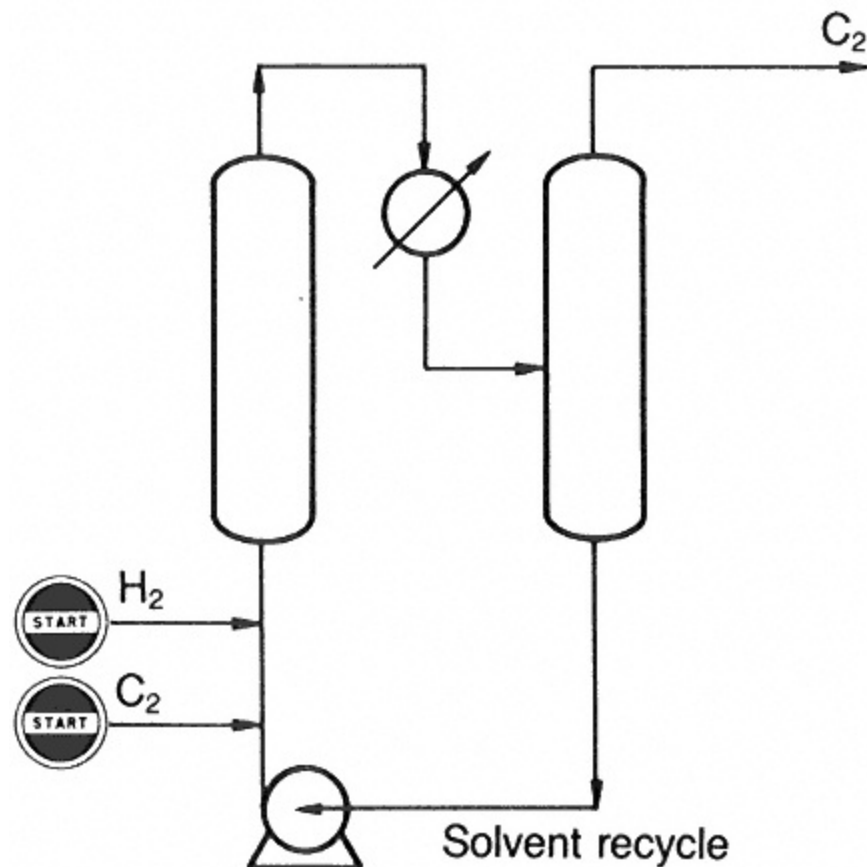


Fig. 7.
Simplified flow sheet for new C2 hydrogenation process.

TABLE 3 Economics of Selective Hydrogenation of Acetylene

C2 hydrogenation: economic balance:

Base: 320,000 t/yr ethylene production

Capital expenses (battery limits) for plant revamping:

\$385,000

Utilities balance: (annual saving):

	\$
hp steam: 3,880 t at \$13/t	50,440
Electricity: 132,496 kWh at 2¢/kWh	26,500
Process water: 2,563 m ³ at \$0.40/m ³	1,025
Cooling water: 959,504 m ³ at 2¢/m ³	19,190
Fuel: 1,092 t at \$200/t	218,400
Utilities total savings:	315,555
Fixed costs (deficit)	(164,900)
Catalyst inventory saving	17,000
Excess ethylene production: 728 t at \$510/t	371,280
Regeneration cost savings	50,000
Total balance	558,935
Profit after taxes	294,467
Pay-out time	16 months

Ethylene yield increase by 1% more for an acetylene content in feedstock of 1.5%

Expected 18-month-cycle length that avoids costly and troublesome frequent regenerations of the traditional process

Higher space velocity, i.e., lower catalyst inventory

Table 3 summarizes a few economics for the revamping of an existing unit to a new one with the new technology. These economics present a balance around the steam cracker, the produced ethane being recycled to the cracker in both cases. As can be seen from Table 3, the new process produces more ethylene at a lower cost (less utilities are consumed in the ethane recycle) with smoother operation (fewer reactor shutdowns for regeneration).

Steam Cracking C3 Cut

Selective hydrogenation of the propylene-rich cut is mandatory for highpurity propylene production. This cut contains some methylacetylene and propadiene (MAPD) which must be removed. Partial hydrogenation of both methylacetylene (propyne) and propadiene gives propylene which results in olefin yields generally higher than 100%. Increasing this yield is economically more and more interesting. Figure 8 shows the improvement obtained with a

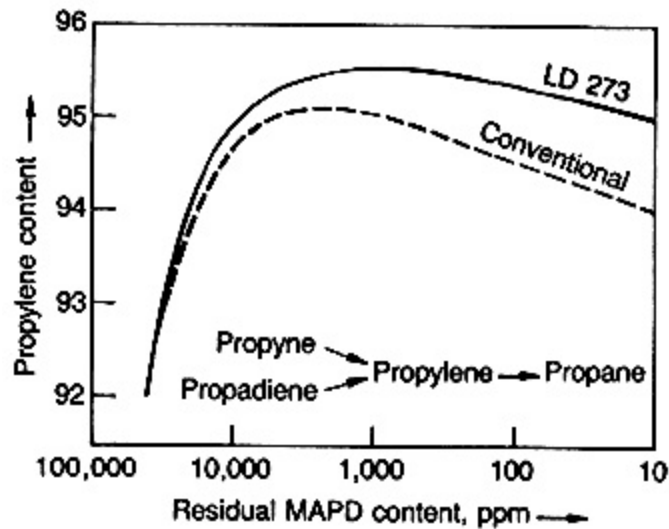


Fig. 8.

Improvement of propylene gain with LD 273.

new promoted palladium catalyst (LD 273) that contains palladium plus a second metal deposited on an inert alumina. With this catalyst the propylene yield obtained with 4 wt.% MAPD in the feed and 10 ppm MAPD in the product is increased to 103.3%.

A second improvement concerns the side reaction of polymerization. As mentioned above for C₂ hydrogenation, oligomerization also occurs to a limited extent in C₃ hydrogenation. In the gaseous phase this side reaction results in catalyst deactivation by progressively plugging the catalyst. In the liquid phase this deactivation does not occur but some C₆ olefins together with a few C₉ olefins are formed. Figure 9 shows that the oligomers formation is drastically reduced with the LD 273 catalyst.

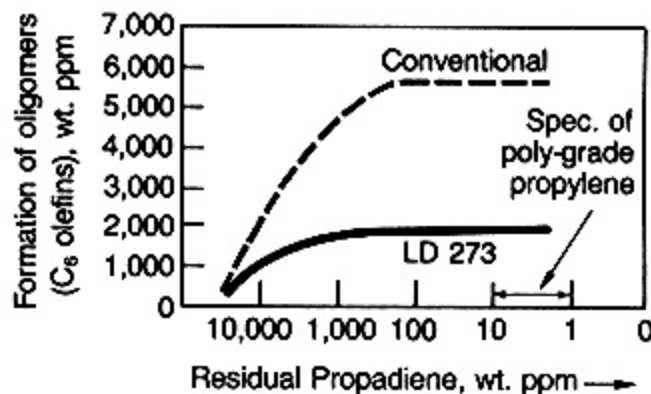


Fig. 9.

Decreased oligomerization activity of LD 273.

Butadiene-Rich Cut

The C4 butadiene-rich cut is usually processed in a butadiene extraction plant. Up-to-date technologies do not require the preremoval of acetylenics (mainly vinylacetylene VAC) but economics for butadiene recovery favor front-end VAC removal. Unfortunately, a specific phenomenon occurs with a conventional palladium catalyst. VAC combines so strongly with the metal that palladium dissolves in the hydrocarbon stream. If VAC hydrogenation is almost complete, palladium is transferred progressively to the very bottom of the catalyst bed. If VAC hydrogenation is only partial, i.e., 70-80% as economics would favor, the reactor effluent does carry over palladium. As a result, catalyst life is not several years but usually a few months or even weeks.

Up to now, all commercial conventional palladium catalysts have had this severe disadvantage. How the new LD 277 catalyst contrasts with these is shown in Fig. 10. Here we report commercial results of palladium losses obtained on two cuts, (1) the raw butadiene-rich cut (VAC = 1.5 wt.%) and (2) the acetylenic concentrate coming from butadiene extraction (VAC = 58% after dilution by hydrogenated product recycle). We see that the palladium losses for both the LD 277 and conventional catalyst are proportional to the average VAC concentration in the reaction $(VAC_{in} + VAC_{out})/2$. It must be pointed out that the palladium loss of the standard catalyst is 10 times as much as the LD 277. On the raw cut the palladium loss of the LD 277 is almost negligible, while it is still very high on the conventional catalyst.

The Process

Ten years ago, hydrofining the C4 cut of the olefin plant in order to contribute to butadiene recovery was not valid. We now know the problem faced when using conventional Pd catalysts and, in addition, extraction

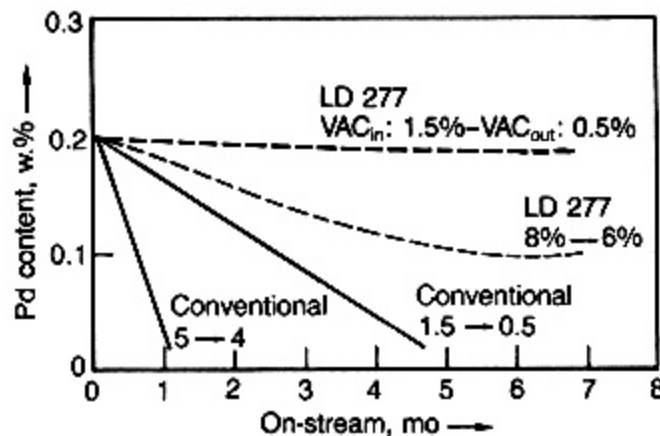


Fig. 10.
Palladium losses from LD 277 and conventional catalysts.

technologies are now able to process nonhydrogenated C₄ cuts. A stable palladium catalyst does exist and the severity of steam cracking has increased. The C₄ raw cut contains much more VAC (now 1.2 wt.%, before 0.5 wt.%), which results in more butadiene losses in the acetylenics extraction stage (acetylenics are withdrawn in a butadiene-rich mixture).

The availability of a stable palladium-based catalyst allowed I.F.P. to again work on the selective hydrogenation of acetylenics in C₄ butadiene-rich cuts with several accomplishments:

Partial hydrogenation of acetylenics and recycle of the unconverted acetylenics-rich stream as it is withdrawn in the downstream extraction unit Selection of proper operating conditions.

Partial Hydrogenation and Recycle

The hydrogenation rates of acetylenics and butadiene are not very different. Thus the selectivity is not high enough to tolerate a complete or nearly complete hydrogenation of acetylenics because of excessive and uneconomic butadiene losses.

Therefore, the realistic concept is to perform a moderate hydrogenation and to recycle the residual acetylenics-rich stream at the inlet of the hydrogenation unit. Such a moderate conversion avoids butadiene losses. The butadiene recovery is drastically improved because purges of butadiene-rich fractions are eliminated.

Figure 11 shows this point. Computer calculations, checked by operation of commercial units, demonstrate that partial hydrogenation performed on a mixture of fresh C₄ with the butadiene-rich extraction drawn off (Case 2) is very interesting and realistic. Butadiene recovery jumps easily to 100% compared to 98% in Case 1 and 97% without hydrotreatment.

Optimization

Operating temperature and hydrogen partial pressure are, together with the liquid space velocity (LHSV), the three key parameters. In the complex mechanism involved in this hydrogenation, the selectivity as defined above and the activity (rate of hydrogenation) are functions of the average hydrogen partial pressure across the catalytic bed. Therefore hydrogen pressure is reduced to increase selectivity, and LHSV is selected accordingly.

Commercial Experience

The I.F.P. process is currently in operation in two olefin plants, and a third load of LD 277 is used in another hydrogenation unit.

Performances are very satisfactory (Table 4). Butadiene losses do not occur across the hydrogenation reactor because of the moderate conversion

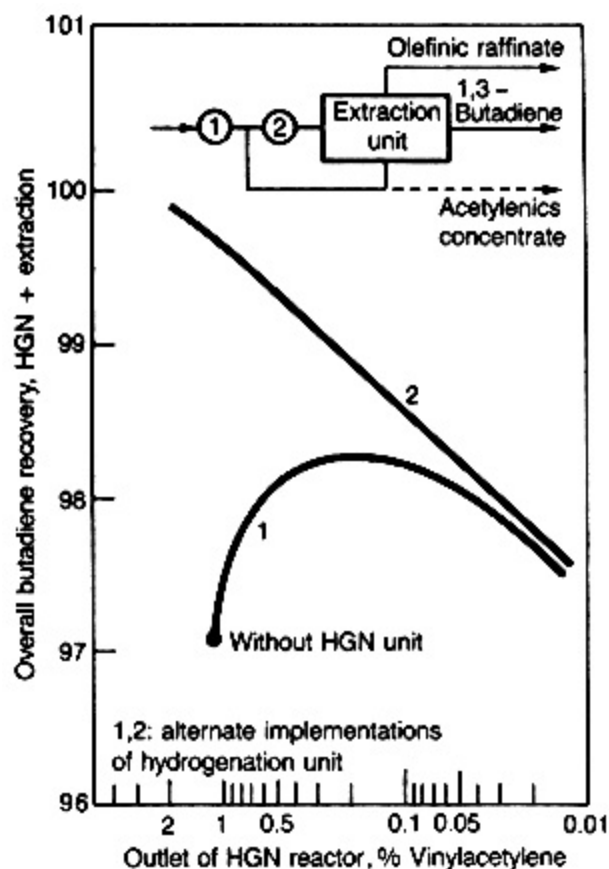


Fig. 11.
Influence of hydrogenator location on global selectivity.

TABLE 4 Performances of LD 277
(VAC hydrogenation in butadiene-rich cuts)

wt. %	Feeda	Product
C3 (ppm)	<100	<100
Isobutane	3.65	2.98
n-Butane	4.45	4.50
1-Butene	11.8	12.65
Isobutene	23.6	23.40
trans-2-Butene	4.10	4.85
cis-2-Butene	2.90	3.70
1,3-Butadiene	45.8	45.80
1,2-Butadiene	0.395	0.35
1-Butyne	0.975	0.81
Vinylacetylene	2.18	0.87
C5+ (ppm)	680	850

aReactor feed: C4 raw cut mixed with acetylenics concentrate recovered in downstream butadiene extraction.

TABLE 5 Improving Butadiene Recovery

	Butadiene plant streams (wt.%)		
	VAC	Acetylenics+ Allenics	1,3-Butadiene
C4 raw cut	1.2	1.6	49
1,3-Butadiene		15 ppm	100
Olefinic raffinate			0.3
Acetylenics concentrate	30	50	50
Performances (butadiene recovery):			
Without HGN unit:	95.97		
With HGN unit:	99.7		
Economics of a 100,000 t/yr HGN unit:			
Investment	US\$700,000		
Propylene cooling	0.8 t/h		
Catalyst	\$2/h		
Electricity	2 kWh/h		

of acetylenics as well as the more favorable acetylenics/butadiene ratio in the feed. Therefore, overall butadiene recovery is almost 100%, the only loss being due to the butadiene content of the raffinate. Commercial operation demonstrates that, as expected from computer calculations based upon the relative reactivities of the hydrocarbons involved, no buildup of any acetylenics or 1,2-butadiene occurs.

Performance of the new catalyst is very attractive. In one plant the catalyst was loaded in May 1983 and is operating as per Table 4 (average VAC content is 1.7%). After 18 months and a few polish burnings, stability is excellent as demonstrated by an almost unchanged selectivity. In the other plant, where the average VAC climbs up to 7%, the catalyst is still in operation 10 months after loading.

These interesting commercial data result in the favorable economics gathered in Table 5. Selective hydrogenation of acetylenics combined with downstream butadiene extraction is back in the picture of optimized olefin plants.

1-Butene-Rich Cut

After butadiene extraction, the C4 cut produced in the steam-cracking operation is an attractive source of 1-butene. End uses of 1-butene require a very low content of butadiene which requires mandatory selective hydrogenation.

More Selective Catalyst

When conventional palladium-based catalysts are used to hydrotreat 1-olefin-rich cuts, a secondary reaction occurs to some extent, i.e., the double bond shift reaction:



This property is a characteristic of palladium which has a high hydrogenation activity but is also very active for the double bond shift reaction as shown by this classification: $\text{Fe} \approx \text{Ni} \approx \text{Rh} > \text{Pd} > \text{Ru} > \text{Os} > \text{Pt} \approx \text{Ir} \approx \text{Cu}$. The less-active metals for isomerization (Pt, Ir, and Cu) are also less active for diolefin hydrogenation. Thus, changing the metal from palladium to another one would not solve this specific selective hydrogenation problem. The best way to obtain good selectivity while keeping good hydrogenation activity is to modify the palladium by the addition of a second metal which changes palladium's electronic properties.

For this purpose, we developed the LD 271. The following data show the intrinsic selectivity of this promoted palladium catalyst compared to a conventional catalyst.

A feed coming from a butadiene extraction plant (C4 raffinate No. 1) is treated in a bench scale unit at various hydrogen-to-butadiene ratios to determine the variation of the 1-butene content as a function of residual butadiene in the product. The results obtained are plotted in Fig. 12. Analysis of the feed and products obtained for a butadiene residual content of 5 ppm is given in Table 6.

We can see that, for the required residual butadiene content, the 1-butene yield on LD 271 is 100% while it is only 94.6% on the conventional palladium catalyst.

Figure 12 shows the effect of increasing the extent of hydrogenation on the feed given in Table 6. The points are experimental results and the curves are theoretical. They correspond to the scheme shown in Fig. 12. According to this scheme, 2-butenes can be formed either by direct hydrogenation of butadiene or by isomerization of 1-butene. By applying the kinetic method, theoretical curves were calculated [32]. They can be seen to fit the experimental points very well. We again observe in Fig. 12 that the LD 271 catalyst has a much higher selectivity than the conventional catalyst.

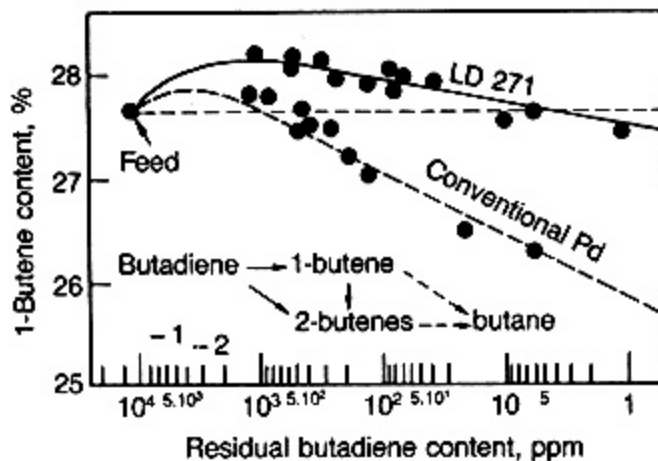


Fig. 12.
1-Butene selectivity improvement with LD 271.

TABLE 6 Feed: C4 Cut (raffinate No. 1) from Napththa Cracking

	wt.% in Feed	wt.% in Product with Conventional Catalyst	LD271 Catalyst
Isobutane	1.5	1.53	1.52
n-Butane	4.3	4.8	4.70
1-Butene	27.70	26.20	27.70
cis-2-Butene	8.60	9.24	8.65
trans-2-Butene	11.55	12.86	12.22
Isobutene	45.20	45.17	45.18
1,3-Butadiene	1.15	5 ppm	5 ppm

1-Butene Yields

For a given catalyst selectivity and a given residual butadiene content, the 1-butene yield will vary as a function of 1-butene and 1,3-butadiene in the feedstocks. Using the kinetic model [26] we calculated theoretical curves representing the 1-butene yield as a function of the 1,3-butadiene content. For a given 1-butene content in the feedstock, we obtain a theoretical network where each curve corresponds to a given product specification (residual butadiene in ppm).

Figure 13 shows two theoretical networks: one for raffinate No. 1 (1-butene = 27.7 wt.%), and another for raffinate No. 2 (after isobutene extraction; 1-butene = 49.1 wt.%). The points are experimental and we can see that they fit well with the theoretical curves, thus showing the validity of the kinetic model.

Impurities and Feedstocks

When a new catalyst is developed, it is very important to check its tolerance to the various impurities which can be present in the different feedstocks. This study has been performed for the LD 271 catalyst. For common impurities like sulfur compounds, the poisoning effect is the same for LD 271 as for the standard palladium catalyst. This poisoning results not only in an activity decrease but also in a drastic selectivity decrease that results in a lower 1-butene recovery.

Some impurities could be put intentionally in the feeds in order to improve the hydrogenation selectivity. This is the case of carbon monoxide that is present in the nonmethanated hydrogen gas coming from steam cracking. In some cases the methanation is bypassed in order to have some CO in the hydrogen gas to the hydrotreater. For example, this injection of CO is often practiced in C2 cut selective hydrogenation because this impurity, while decreasing the apparent activity, is claimed to improve the ethylene yield. Similarly, CO addition is claimed [33,34] to improve the 1-butene yield in butadiene hydrogenation. Figure 14 shows the effect of CO addition on a standard palladium catalyst.

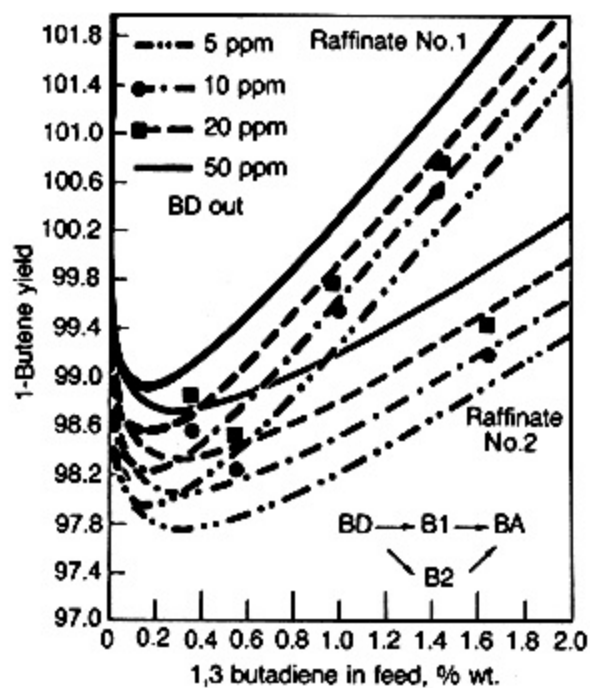


Fig. 13.
1-Butene selectivity for hydrogenation of raffinate No. 1 and raffinate No. 2.

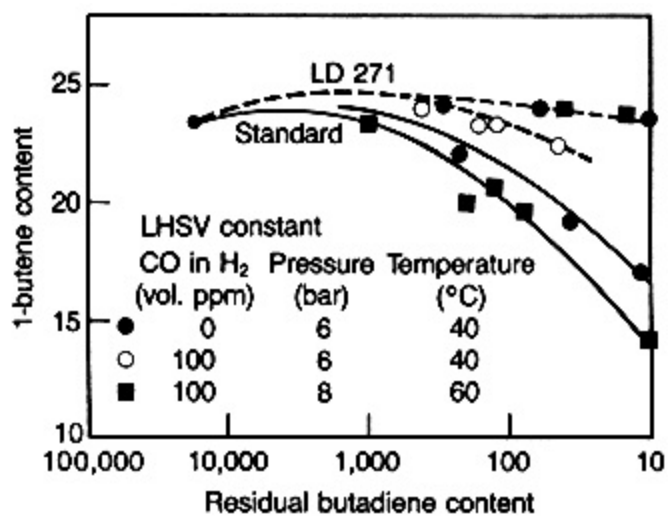


Fig. 14.
Influence of carbon monoxide on 1-butene selectivity.

The injection of 100 ppmv in the hydrogen does not improve the 1-butene yield. The effect is rather detrimental on the selectivity of the catalyst; the addition of CO is far from being a wise recommendation because the yield curve with CO is lower than without CO. The same effect of selectivity depression is obtained on LD 271. It is nevertheless possible to recover the normal selectivity by increasing the operating temperature. The pressure is increased accordingly to maintain the hydrogen partial pressure. In any case, CO addition cannot change the nature of the catalyst.

Many contaminations can originate from the different treatments undergone by the C4 cut. For example, the C4 cut freed of isobutene (raffinate No. 2) can come from several processes which are listed in Table 7.

Extensive studies have been made by I.F.P. in order to determine the tolerance to these various impurities. In addition, long duration tests have been performed on the feeds coming from these various processes. We have observed that no deactivation occurs.

New Process

This hydrogenation is performed over LD 271 in the liquid phase to save vaporization and condensation energy, and at low temperature because the hydrogenation rate constant of butadiene, in noncontaminated fractions, is high. Therefore, a low operating pressure may be used.

Hydrogen partial pressure is an important factor. Too fast hydrogenation of butadiene induced by a high hydrogen pressure may lead to mass transfer limitations that would result in a decrease of the selectivity. Therefore, a low hydrogen pressure is used and the space velocity (LHSV) is selected accordingly in order to get the requested conversion level.

Commercial Experience

The first I.F.P. commercial plant for this specific hydrorefining started in 1978, with a conventional palladium catalyst, for a United States 1-butene producer. In 1983 the demand for 1-butene increased enough to justify the

TABLE 7 Raffinate No. 2 Impurities

Process	Specific Impurities
Isobutene selective catalytic dimerization	None
Isobutene polymerization (butyl rubber)	Alkyl chlorides
Isobutene extraction with H2SO4	Alkyl sulfates
Isobutene extraction by MTBE synthesis with methanol	Methanol, ethers

TABLE 8 Steam Cracking C4 Raffinate No. 2 Hydrogenation

Liquid vol. %	Feed	Hydrogenated Product
Propane propylene	0.16	0.15
Isobutane	11.40	11.35
n-Butane	18.40	19.05
1-Butene	43.60	42.20
Isobutene	0.08	0.08
cis-2-Butene	10.80	11.27
trans-2-Butene	14.80	15.85
1,3-Butadiene	0.71	6 ppm
C5	0.05	0.05

I.F.P. licensee to switch to the improved catalyst. LD 271 was loaded in the last quarter of 1983 and successfully started. In early 1985 the first cycle was still going on. During this 14-month period of processing an MTBE raffinate, one hot hydrogen stripping was the only activity recovery procedure to be performed. Typical performances of this large-scale commercial plant are presented in Table 8.

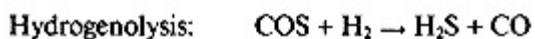
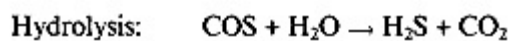
Contaminated LPG Fractions

FCC C3 and C4 cuts are much more contaminated than similar fractions from steam cracking because the usual processing for motor fuel production is far less compelling. Therefore, these fractions are not always suitable for conventional palladium catalysts.

Moreover, the trend to chemical use of these FCC effluents is concomitant with the diversification of crudes origins. Many new crudes contain contaminants (e.g., arsenic) which are lethal for any catalyst.

In this particular case the catalyst, whatever it is, must be protected from poisoning by the addition of guards upstream of the hydrogenation reactor.

As far as sulfur compounds are concerned, H₂S is a poison but it is easily removed by standard refining processes (amine wash, caustic wash, etc.). After such treatment, FCC C3 fractions still contain some COS which is not, as such, a poison, but which can decompose into H₂S by two possible reactions:



The first reaction of COS with water is not promoted by the metal, and any surface where water and COS can coadsorb promotes the decomposition.

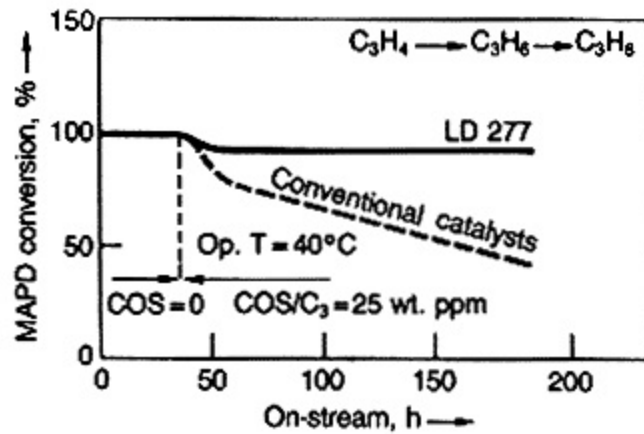


Fig. 15.
Hydrogenation of COS-contaminated C3 cut.

Consequently the only way to eradicate this reaction is to dry the hydrogenator feedstock. This drying is normally required for many downstream processing steps, e.g., Dimersol, alkylation, etc.

The second reaction, hydrogenolysis, is by contrast specifically promoted by the highly dispersed metal of the catalyst. More precisely, the palladium of the conventional catalyst activates the decomposition of COS into H₂S and produces self-poisoning. The solution to this problem requires a deep modification of the palladium properties. This has been accomplished through alloying. The new promoted catalyst, LD 277, offers the unique property of remaining stable while processing C₃ fractions containing COS.

Figure 15 illustrates the stability of LD 277 when confronted with such organic contaminants. This advantage has been proven with long duration tests performed on standard FCC C₃ and C₄ fractions in a pilot plant implemented on-line with a commercial FCC unit. Figure 16 shows such a test on a C₄ cut. On LD 277, the product can be seen to meet specification during 90% of the running time. On the contrary, with the conventional catalyst, this period is only 50% of the time. More precisely, in the same operating conditions, LD 277 can accept a feed containing up to 30 ppm of sulfur, while the conventional catalyst must be discarded for a sulfur content exceeding 15 ppm. Based on these successful tests, the operator decided to load this new catalyst.

Pyrolysis Gasoline

One-stage selective hydrogenation is used to improve the stability of raw gasoline, i.e., increase its induction period and lower its gum content without altering its marketable value, i.e., its octane number.

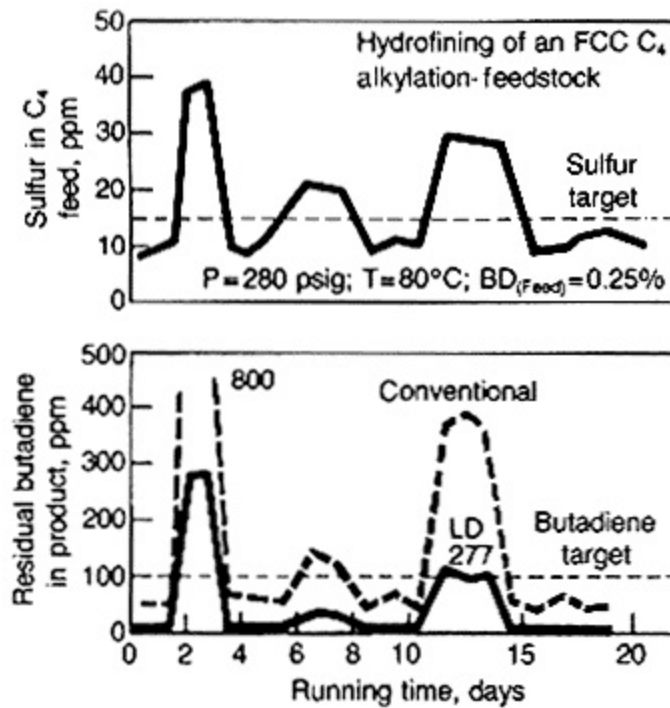


Fig. 16.
Sidestream pilot test on FCC C4 cut.

The process achieves selective hydrogenation of diolefins, alkenylaromatics, and dimers such as dicyclopentadiene and methyldicyclopentadiene without contributing to undesirable side reactions (polymerization and olefins saturation).

The new palladium catalyst has higher activity than nonpromoted palladium catalysts for the selective hydrogenation of pyrolysis gasoline.

Such naphthas contain a few hundred ppm of sulfur, with 80% being thiophene, but also a few ten ppm of other types of sulfur compounds (sulfides, disulfides, and even some H_2S). Extensive research performed in our pilot plants, as well as feedback from commercial units in operation, enable the inhibiting effect of the various sulfur compounds to be rated as follows when the operating temperature is in the range of $100^\circ C$:

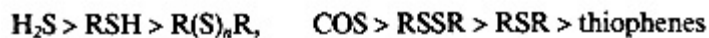


Figure 17 illustrates the superiority of the LD 275 catalyst compared to a conventional palladium catalyst with the same palladium content.

Figure 18 shows a pilot-plant test under severe conditions (high space velocity) with a feed coming from a high-severity steam cracker. We can see that, on LD 275, conversion remains almost steady, with a moderate increase in the reaction temperature after about 300 h. A continuous and rapid increase of the reactor temperature is needed for the conventional catalyst, while diene conversion drops slowly but regularly.

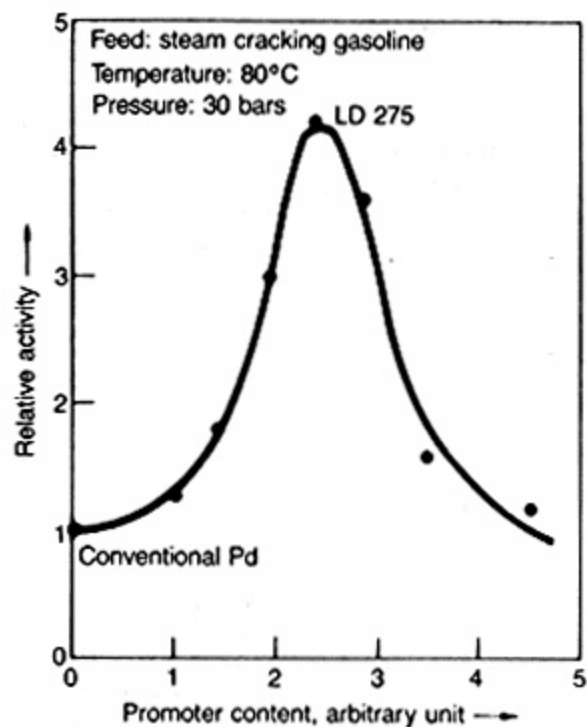


Fig. 17.
Effect of promoter content on diene hydrogenation rate.

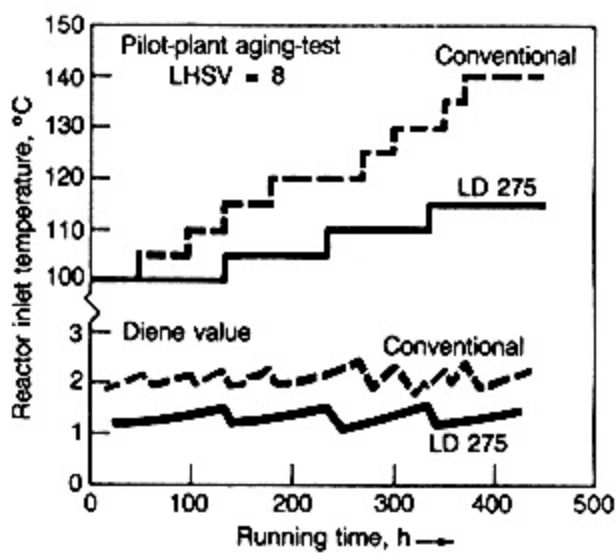


Fig. 18.
Aging test of LD 275 in pyrolysis gasoline hydrogenation.

Conclusion

A new generation of hydrogenation catalysts, bimetallic palladium catalysts, is now available. They meet the very stringent requirements of a new refining and petrochemical industry that has to face a difficult economic period in which the highest performance becomes standard. Therefore, the demand for these new, very efficient catalysts and their associated technologies is rapidly growing.

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Isomerization*

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T. Wheeler,
and F. G. McWilliams

Introduction

Isomerization is a shift in the configuration of a molecule, without change in the number of atoms present. There are three main classes of hydrocarbon isomerization: structural, geometrical, and optical.

Commercial applications of isomerization generally reflect structural changes in order to create a molecule that is more reactive, has a higher performance level, or has a more desirable property than the other isomers. The following examples of major commercial isomerization reactions are discussed in this article.

*UOP, Parex, Butamer, Penex, Molex, Platforming, and Isomar are registered trademarks and/or service marks of UOP Inc. Tatoray is a service mark of Toray Industries, Inc.

Feedstock	Product Objectives
Aromatic isomerization:	
Xylene isomeriation	Modify natural distribution to meet market demands
Paraffin isomerization:	
C4 Paraffins	Tertiary carbon which is more reactive
C5/C6 Paraffins	High octane motor fuel

Isomerization may also occur as part of a complex reaction mechanism (such as naptha reforming) and can be used to control the ultimate production distribution. There are many other examples of isomerization in the specialty chemical production and in the pharmaceutical industry, but because of the variety of applications it is beyond the scope of this discussion to give any details.

Isomerization of C8 Aromatics

Background

p-Xylene and o-xylene are important petrochemical intermediates for such products as polyester fiber and film, plasticizers, aramids, polyesters, and alkyd resins. These intermediates typically are recovered from mixed C8 aromatics by means of crystallization (or, in the more modern plants, through adsorption). The C8-aromatics stream is obtained principally by catalytically reforming straight-run naphtha, followed by fractionation to separate lighter and heavier aromatics.

The isomer distribution of C8 aromatics from catalytic reforming does not closely match the demand pattern (Table 1).

A recovery process alone would not fully utilize the valuable C8-aromatics stream, as most of the product would consist of a m-xylene and an ethylbenzene-rich raffinate. In order to obtain high yields of p-xylene and o-xylene, the raffinate must be isomerized to reestablish a near-equilibrium distribution of xylene isomers.

Isomerization in Xylenes Complex

A C8-aromatics isomerization unit is usually associated with a xylenes recovery unit. A typical combination of isomerization and recovery units is shown in Fig. 1.

TABLE 1

Typical	Worldwide
---------	-----------

p-Xylene	C8 Aromatics	Demand
m-Xylene	42%	Negligible
o-Xylene	22%	30%
Ethylbenzene	16%	a

aEthylbenzene for styrene production generally is obtained by benzene-ethylene alkylation.

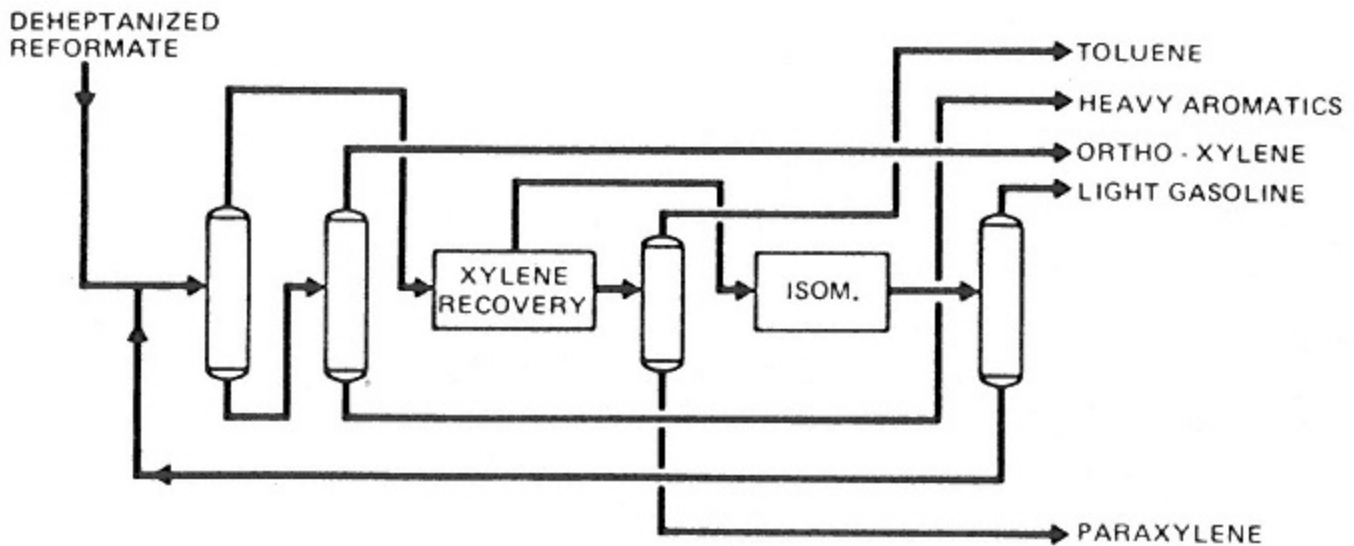


Fig. 1.
Integrated xylene complex.

C₈ and heavier aromatics from catalytic reforming are fractionated to separate the desired amount of the higher boiling o-xylene from the other C₈ isomers. Pure o-xylene is recovered by further fractionation to remove C₉ and heavier aromatics.

The overhead stream is sent to the p-xylene recovery unit, either fractional crystallization or adsorption. Typically, crystallization recovers about 65% of the p-xylene, while recovery in an adsorption unit is about 98%.

The raffinate from the p-xylene recovery unit is sent to isomerization, which reestablishes a near-equilibrium mixture of isomers. After stripping to remove light ends, isomerized product is returned to the recovery section.

Process/Catalyst Alternatives

A critical factor in the isomerization of C₈ aromatics is the conversion of ethylbenzene. Isomerization processes and catalysts may be classified according to their approach to ethylbenzene conversion.

Older catalyst systems, still in use in some units, have very low ethylbenzene conversion. Ethylbenzene builds up in the recycle loop between the recovery and isomerization units until the proportion converted matches or even exceeds that in the fresh feed. A fresh feed fractionator is typically needed to remove ethylbenzene and limit its buildup in the recycle loop. This fractionation results in higher processing costs.

An alternative catalyst system isomerizes ethylbenzene to xylenes to obtain a near-equilibrium xylene mixture. The conversion of ethylbenzene to xylenes is such that only a minor portion is converted to lighter aromatics. The main difference between the latter two systems is that isomerization of ethylbenzene to xylenes requires the use of a noble metal catalyst, usually platinum, supported on a heterogeneous acidic catalyst base, in the presence of a hydrogen atmosphere. It is postulated that the isomerization of

ethylbenzene to xylenes takes place through a naphthene bridge arising from the partial saturation of the ethylbenzene aromatic ring. It is indeed known that a certain level of C₈ naphthenes must be maintained in equilibrium for the isomerization of ethylbenzene to xylenes.

If isomerization of ethylbenzene to xylenes is not required, the isomerization of xylenes can be accomplished over a variety of heterogeneous acidic

catalysts, usually also in the presence of a hydrogen atmosphere. Acid exchanged zeolites and other catalysts can be used for this purpose. Ethylbenzene reacts in various ways over these catalysts. Whereas ethylbenzene disproportionation is a significant factor over some catalyst systems, dealkylation of ethylbenzene to benzene is perhaps more common over modern catalyst systems designed for high-severity operation at higher temperatures. Although not designed for the isomerization of ethylbenzene to xylenes, some of these catalysts may also contain levels of platinum and other metals.

It is also possible to dealkylate ethylbenzene as a means of controlling its concentration in the recycle loop. This is done at significantly higher temperatures, yielding principally benzene from the converted ethylbenzene while isomerizing xylenes. Recycle rates with ethylbenzene in the system are reduced significantly but overall xylene product yields are lower.

Process Description

One example of a xylene isomerization technique is the UOP Isomar process. This process uses a specially formulated catalyst to isomerize ethylbenzene as well as xylenes to an equilibrium xylene mixture with minimal ring loss.

The very simple process flow scheme is shown in Fig. 2 and is similar to that used in other C₈ aromatic isomerization processes. The raffinate stream from p-xylene recovery is combined with makeup and recycle hydrogen, heated by exchange with the effluent and a fired heater, and charged to the

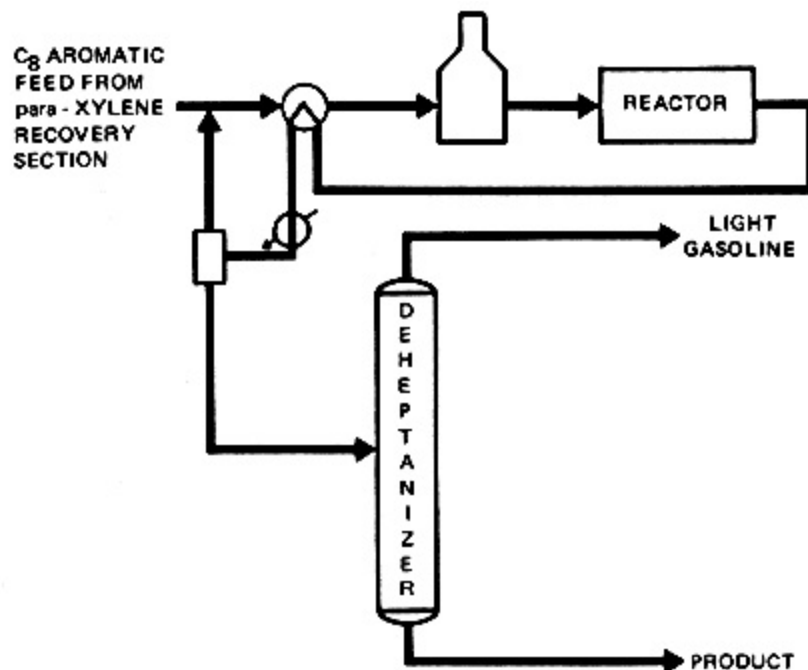


Fig. 2.
Isomar process.

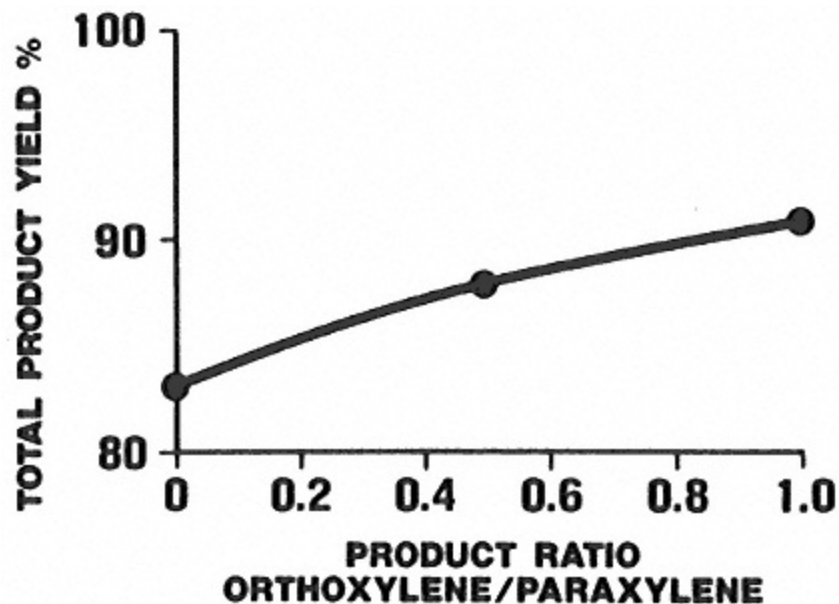


Fig. 3.
Typical Parex/Isomar yield structure. The Total Product Yield % (ordinate) is the sum of o-xylene and p-xylene product divided by C8 aromatic content of fresh feed in weight percent.

isomerization reactor. Reactor effluent is heat exchanged and cooled, and the vapor and liquid phases are separated with hydrogen-rich vapor being recycled to the reactor.

Separator liquid is charged to a deheptanizer, from which lighter by-products are taken overhead. Small quantities of heavy aromatics in the deheptanizer bottoms are removed by recycling of this stream to the fractionator column, as shown in Fig. 1.

Yields

Product yields within the xylenes complex are dependent on the quantity of o-xylene produced. As more of the ortho isomer is removed as product, the size of the recycle stream is reduced. This results in fewer passes through the Isomar unit, and hence less xylene loss due to transalkylation and cracking. Figure 3 shows the effect of the product ratio on the total product yield. The combined yields of the ortho and para isomers range from 83.84% for all p-xylene product to 91% for equal quantities of para and ortho. These yields reflect the total amount of C8 aromatic isomers recovered ratioed to the total amount of C8 aromatics contained in the feed.

By-products from the complex are C9 and higher aromatics, light gasoline, high purity (nitration grade) toluene, and small quantities of fuel gas. All by-products are of relatively high value, and pose no disposal problem. The C9+ aromatics can be sold as solvent or used as a high octane blending component in gasoline. The toluene is readily saleable, and the light gasoline can be used directly in the gasoline pool. The fuel gas can be used within the complex as fuel for fired heaters.

The toluene and C9+ aromatics can also be combined and fed to a transalkylation, Tatoray, unit [6] for the disproportionation of aromatics. This allows these streams to be

reconverted to xylenes, thus improving overall

TABLE 2 Typical Utility Consumption for Parex/Isomar Fractionation Complex

[Basis: 61,300 lb/h xylene products (500 million lb/yr)]

Ortho/para product ratio	0	1.0
Net utility consumption for complex:		
Power, kW	3200	1150
Fuel fired, 106 Btu/ha	240	245
Cooling water, gal/min	100	100
Products, 106 lb/yr:		
p-Xylene	500	250
o-Xylene	0	250
Estimated erected cost, ^b \$106	75	70

^aNet heating value.

^bIncludes initial catalyst, adsorbent and desorbent inventory.

yields. By using this scheme, p-xylene yields in excess of 89% can be obtained and proportionately higher yields are also obtained when both p- and o-xylene are recovered.

Utilities

Utility consumption is also affected by the ortho/para product ratio. As the relative quantity of o-xylene increases, the utility consumption in the Parex and Isomar units decreases while the fractionation utilities increase. The net result is that power consumption decreases greatly, and fuel use increases very slightly with increasing o-xylene production. Table 2 provides a comparison of 100% p-xylene production with the para/ortho operation.

There is a large degree of heat integration within the xylene complex. Typically, the xylene fractionator is operated at high pressure (150 lb/in.² gauge) to allow the condensing overhead vapor to supply heat to reboil other columns. This column can thus supply most of the heating requirements for the entire complex without seriously affecting operating flexibility.

Capital Costs

Battery limits erected costs are shown in Table 1. These costs include the Parex and Isomar units, a xylene fractionator and an o-xylene recovery column. The initial inventories of adsorbent, desorbent, and catalyst are also included.

Economics

Since the C₈-aromatics isomerization unit is always part of a xylenes complex, its economics cannot be considered in isolation. For illustration of

economic variables, the adsorption recovery scheme has been used in a Parex/Isomar complex based on Fig. 1.

A summary of the process economics for the same two cases is shown in Table 3. All the prices for feeds, products, and utilities are subject to fluctuation because of market conditions. The values used in this evaluation are estimated "stable market" prices projected in 1985. It should be noted that often an intermediate value of the o-/p-xylene product ratio is more profitable than either of the cases listed. Usually a product ratio of 0.2 to 0.4 will be best in the United States market.

TABLE 3 Process Economics

(Basis: 500 × 106 lb/yr xylene product)

Ortho/para product ratio:	Value ¢/lb	106 lb ⁰	\$106/yr	106lb ^{1.0}	\$106/yr
Products:					
p-Xylene	23	500.0	115.00	115.0	57.50
o-Xylene	18			250.0	45.00
Heavy aromatics	12	50.6	6.07	25.5	3.06
Light gasoline	11	37.7	4.15	18.9	1.78
Toluene	12	16.1	1.93	8.1	0.97
Fuel gas	\$3/106Btu	3.2	0.20	1.6	0.10
Subtotal		607.6	127.35	554.1	108.41
Feedstocks:					
Mixed xylenes	14	602.0	85.55	549.0	77.90
Hydrogen	35	5.6	1.96	5.1	1.79
Subtotal		607.6	87.51	554.1	79.69
Gross margin			39.84		28.72
Operating costs utilities:					
Power, \$0.5/kWh			1.31		0.47
Fuel, \$3/106 Btu			5.88		6.00
Cooling water, \$0.5/103 gal			0.00		0.00
Subtotal			7.19		6.47
Catalyst and chemicals			0.74		0.32
Capital related costs ^a			6.00		5.60
Operating cost subtotal			13.93		12.39
Gross cash flow before taxes			25.91		16.33
Pretax payout of investment, yr			2.9		4.3

^aIncludes maintenance, 3%; insurance and local taxes, 3%; and labor and general overhead, 2%.

Isomerization of C₄ and C₅/C₆ Paraffins

Isomerization of C₄/C₆ paraffins (alkanes) is practiced to create more highly branched isomers from straight-chain (normal) or lesser branched ones.

The first commercial butane isomerization process unit went on stream in late 1941. It was based on using aluminum chloride as a catalyst, and it was characterized by high operating costs and low on-stream efficiency. This was typical for all of the commercial light paraffin isomerization processes available at that time. After further research, a highly active, low temperature, hydroisomerization catalyst was made available to the industry in 1959. This catalyst system, which is now widely accepted by the refining industry, is capable of achieving high paraffin conversion at low temperature. More recent developments of this same catalyst system form the basis of the major part of current light paraffin isomerization processes.

The major historical use of butane isomerization has been in the production of i-C₄ needed for conversion of C₃ and C₄ refinery olefins to high octane alkylate. Increasing amounts of alkylate and hence of i-C₄ are needed as lead usage in gasoline is restricted.

A potentially large demand of i-C₄ has developed in conjunction with the manufacture of MTBE and TBA, which are high octane gasoline blending components particularly useful in lead-free gasolines. The isobutane product is dehydrogenated to the corresponding olefin and then made into the ether or the alcohol. Unconverted butenes and n-C₄ can be recycled to achieve essentially 100% conversion of the feed butanes to MTBE or TBA.

The most widespread use of light paraffin isomerization has been to improve the octane of the refinery light naphtha. Light straight-run naphtha makes up 10-15% of the typical refinery gasoline pool and has a Research clear octane number of about 65-70. In a once-through flow scheme utilized in the low-temperature isomerization process, the octane of this pentane/hexane mixture can be boosted to around 83-85. This, in turn, adds around 1.5-2.5 octane numbers to the gasoline pool. Using a recycle flow scheme, isomerization can add a total of around 2.5-3.5 octane numbers to the pool.

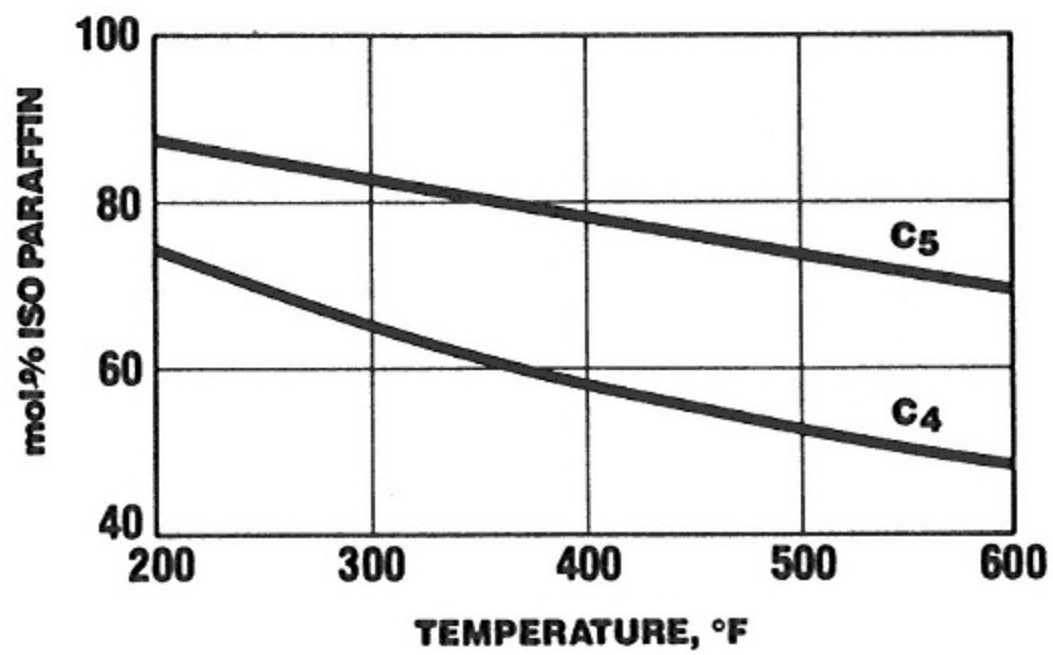


Fig. 4.
Paraffin equilibrium plot.

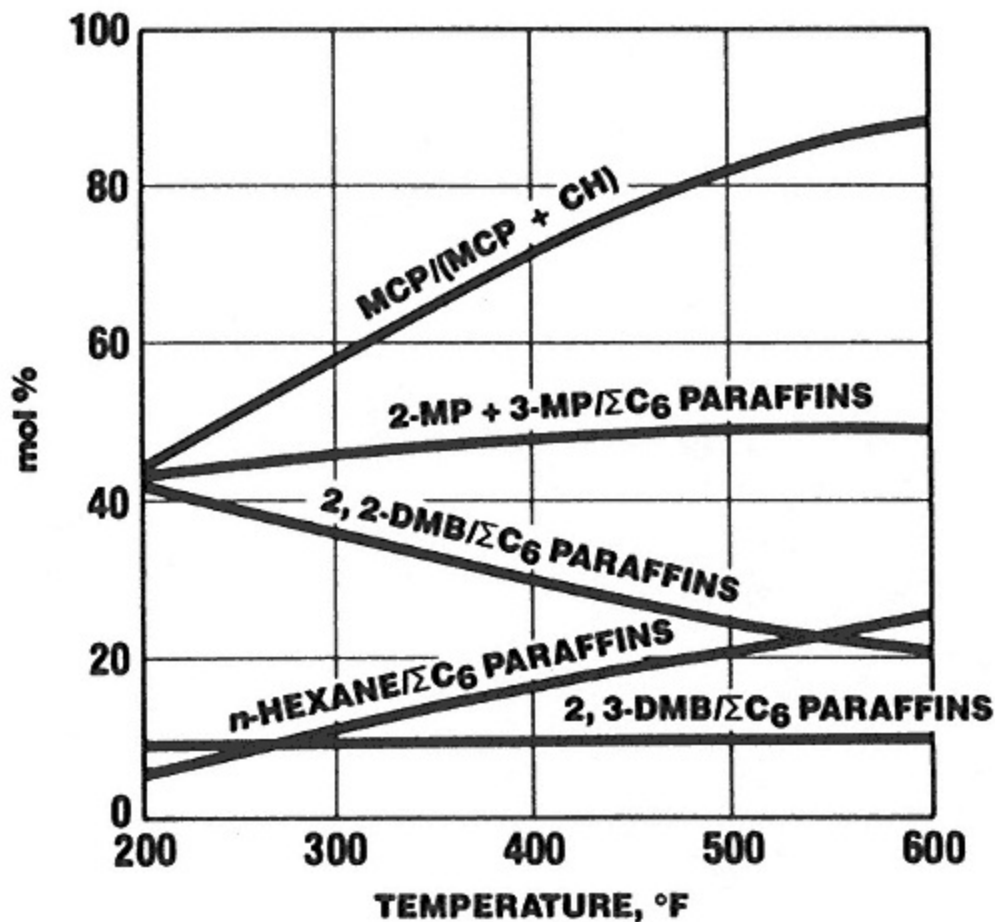


Fig. 5.
C6 fraction equilibrium plot.

Chemistry and Catalysts

Equilibrium Limitations

Chemical equilibrium limits the amount of branched compounds that can be formed in a single pass over the catalyst. Low temperature favors higher conversions, of n-paraffins to the desired branched structures. Historically, the search has been for catalysts with high activity to permit a close approach to equilibrium at as low a temperature as possible. Such extremely active catalysts (allowing operation below 400°F) require that the feedstock be free of contaminants, while less active ones (500-650°F operating temperature) require less costly feedstock purification; both types are used commercially.

The chemical equilibrium, which is independent of pressure, is shown in Fig. 4 for C4 and C5. Actually, there are three possible C5 isomers, but neopentane (2,2-dimethylpropane) occurs only to a very minor extent naturally in petroleum and, since no commercially used catalyst is able to form more than trivial amounts, it is omitted from the graph. Figure 5 displays the equilibrium among the five hexane isomers and includes the equilibrium between cyclohexane and methylcyclopentane, because these are significant, although minor components, in the usual C5/C6 mixture subjected to isomerization. Because of nearly identical octane numbers, only the sum of 2-methyl- and 3-methylpentane is shown. Published equilibrium measurements from various sources are not in complete

accord with each other or with compositions calculated from published thermodynamic functions. However, the temperature trends are unequivocal, and compositions from various sources differ by about 5% at most.

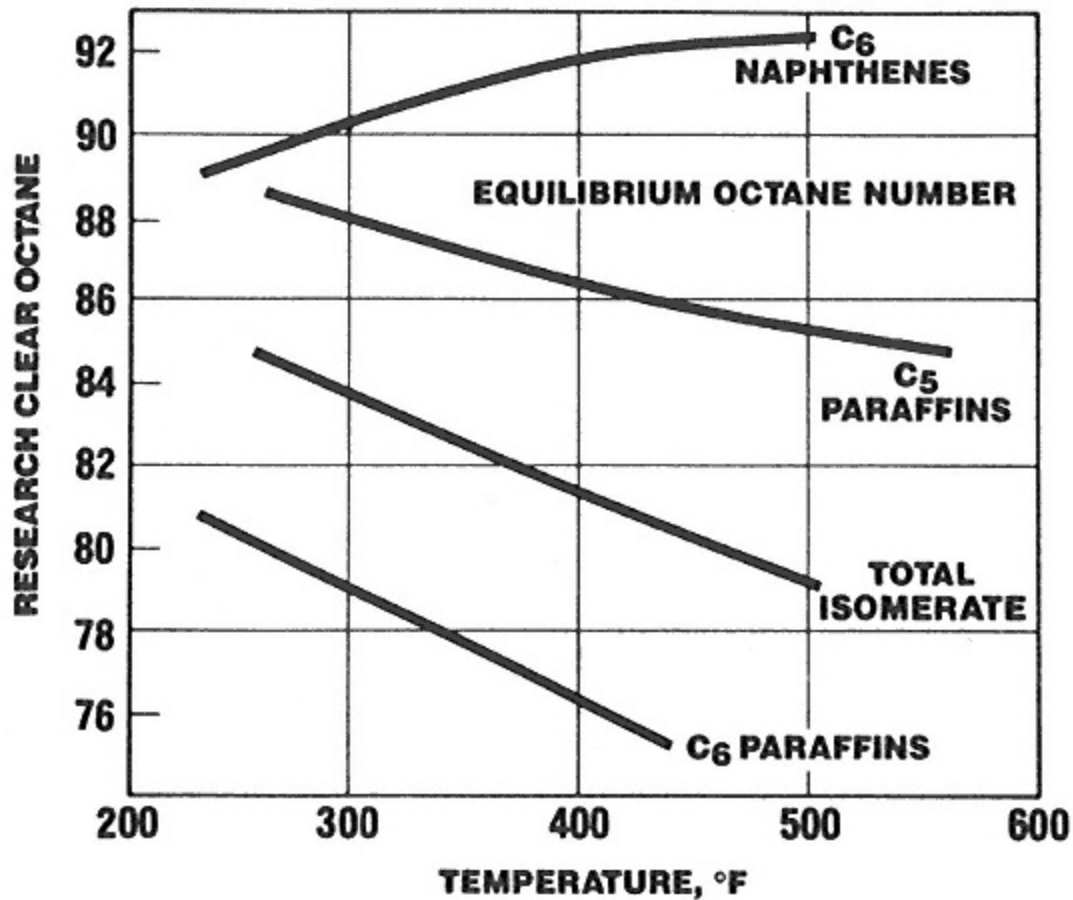


Fig. 6.
Research clear octane number of equilibrium mixtures.

Figure 6 shows the C₅/C₆ equilibrium in terms of Research clear octane number, which is more directly meaningful in petroleum refining. The curve labeled "total isomerate" refers to a typical mixture containing about 40% C₅, 50% C₆ paraffins, and 10% C₆ cycloparaffins (naphthenes).

Catalyst Types and Characteristics

Neuizescu and Dragan [1] showed in 1933 that hexane and heptane are isomerized by aluminum chloride, and Ipatieff [2] reported in 1936 that butane is similarly isomerized. An enormous amount of research on paraffin isomerization has been conducted since these pioneering discoveries. Hundreds of papers and patents have been published describing the kinetics and equilibrium involved, the various catalysts for the reactions, and the effects of poisons and promoters on these catalysts and the reaction mechanisms. At least a score of processes have been developed on the basis of this research, but only a few have actually been built on a commercial scale.

Fortunately, most of the work has been covered in extensive review articles [38], so the emphasis in this writing will be on those processes or catalysts most widely used commercially today.

During the first dozen years after the discovery of paraffin isomerization, many catalysts capable of promoting the reaction were discovered and are described in the literature.

They include molybdenum trisulfide, molybdenum disulfide, molybdenum trioxide, silica, copper, alumina, nickel-alumina, nickel-zinc oxide on charcoal, platinum on charcoal, and sulfuric acid. Generally, these are all less active than Friedel-Crafts catalysts.

It was found that nearly all Friedel-Crafts salts catalyze paraffin isomerization in varying degrees. Among these are aluminum chloride, aluminum bromide, ferric chloride, aluminum admixed with zirconium chloride, copper chloride, zinc chloride, calcium chloride, boron fluoride and hydrogen fluoride with or without metallic nickel present, tin chloride, and zirconium chloride. Of these, the aluminum halides are the most active.

World War II created an urgent need for isobutane for the manufacture of alkylate (an essential ingredient of high octane aviation gasoline), so early research was applied to the construction of 38 plants in the United States and 5 in allied countries. Five distinguishable processes were used, and they all used aluminum chloride in some form [915]. Companies associated with these processes included Shell, Standard Oil Development Company, Universal Oil Products Company (UOP), Standard Oil Company (Indiana), and the Texas Company.

These units fulfilled a wartime need but were plagued by corrosion, plugging, and high catalyst consumption, which resulted in poor on-stream efficiency and high costs. A few "improved" units were built during the 1950s, but the problems persisted. Collectively, these processes are called "first generation" and they do not represent a significant fraction of current unit capacity.

The introduction of the Platforming process by UOP in 1949 and the rapid spread of catalytic reforming dual-functional catalysts in the 1950s focused attention on the development of similar catalysts for paraffin isomerization. Isomerization was known to be one of several reactions occurring during catalytic reforming, and it was a natural step to isolate this reaction for use with feeds where the other reactions are not required.

Research in this area showed that the use of dual-functional (hydroisomerization) catalysts did, indeed, eliminate many of the shortcomings of the first generation Friedel-Crafts systems. It became unnecessary to handle corrosive substances, and the sensitivity toward impurities such as water, sulfur, olefins, and higher paraffins was drastically reduced. These "second generation" hydroisomerization processes supplanted the earlier ones during the middle and late 1950s, but not many units of any type were built in this period because of market-related reasons.

These catalysts generally employ a noble metal as a hydrogenation/dehydrogenation component on high surface area acidic supports such as halided alumina, silica-alumina, and alumina-boria. The cited review articles may be consulted for details. Processes utilizing such dual-functional catalysts were satisfactory in every respect except that they operated at high temperatures and the conversions were severely limited by unfavorable equilibrium; they are little used today.

More recently, catalysts of this type were developed that use crystalline aluminosilicates (zeolites) as supports. These are attractive because they operate at about 200°F lower temperature where the equilibrium is more favorable.

The truly low-temperature, dual-functional hydroisomerization catalysts are called "third generation," even though there is some chronological overlap with the zeolites. These are characterized by greatly enhanced acidity,

which provides the capability of operating at temperatures approximating those used in the early Friedel-Crafts processes but without the problems mentioned. They are generally prepared by treating a platinum-alumina composite with a polyhalide such as carbon tetrachloride, chloroform, methylene chloride, hexachloroethane, aluminum chloride, thionyl chloride, sulfuryl chloride, etc. Some procedures entail preconditioning of the base or posttreatment of the catalyst; the literature is replete with descriptions of manufacturing procedures for specific catalysts.

The first commercial use of this type catalyst appears to be in the UOP Butamer process for C4 isomerization, announced in 1959 [16, 17]. Several years later its application was extended to C5/C6 in the UOP Penex process [18, 19]. Like all third generation catalysts, it is sensitive to sulfur (transient) and to water so the feed must be pretreated and dried. Under normal operating conditions, such a catalyst is long-lived, and runs of several years between catalyst changes are not uncommon.

A second commercialized process utilizing a dual-functional catalyst was announced by British Petroleum in 1964 [20], and described in later papers [21, 22]. Gulf Oil reported on similar catalysts prepared via the use of chlorinated sulfur compounds [23], and Texaco [24] and SNAM s.p.a. [25] have disclosed other "third generation" catalysts.

The "family tree" of the development of paraffin isomerization catalysts shown in Table 4 is adopted from a review paper by Lawrance [5]. The listing

TABLE 4 "Family Tree" of Paraffin Isomerization Catalysts

First Generation: Friedel-Crafts		Second Generation: Hydroisomerization high temperature	
	°F		°F
AlCl ₃ /hydrocarbon complex	250	Platinum/Al ₂ O ₃	850-950
↓		↓	
AlCl ₃ on bauxite or Al ₂ O ₃	100-150	Platinum/Al ₂ O ₃ /SiO ₂	700-850
↓		↓	
AlCl ₃ /SbCl ₅ /HCl	150-210	Platinum/Al ₂ O ₃ /B ₂ O ₃	600-700
↓		↓	
AlBr ₃ /HBr	75-120	Pt/Y-type zeolite	600-650
		↓	
		Pt/mordenite	500-550
		↓	
		Third generation: Hydroisomerization (low temperature)	
			°F
		Pt/Al ₂ O ₃ reacted with AlCl ₃	200-400
		Pt/Al ₂ O ₃ reacted with organic chlorides	200-400

is probably not complete, but it clearly shows the three generations of catalysts that have been discussed. The chronology may be a bit misleading in that all those general types are in commercial use today. Further, zeolitic catalysts like Shell's [26] and UOP's [27] are of recent vintage but are listed under "second generation" because of their higher temperature requirements.

Feedstock Composition

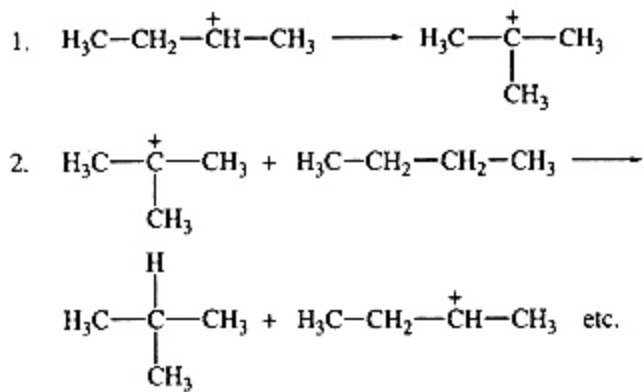
Units announced to date charge C₄, C₅, C₆, or C₅/C₆. While there is nothing about any type of catalyst that precludes simultaneous C₄/C₅/C₆ isomerization, this mode of operation is less than optimal. For a reasonable reaction rate, C₄ requires a higher temperature than the optimum for C₅/C₆. Somewhat more than usual C₆ hydrocracking would be encountered when processing C₄C₆, or else less than maximum C₄ isomerization would have to be accepted. If all three must be isomerized, it may be cheaper to accept some compromise in performance than to build two separate isomerization units.

Reaction Mechanisms

Rarely is there unanimity concerning the mechanism of a chemical reaction, and paraffin isomerization is no exception. Space and objectives of this Encyclopedia do not permit full resolution of disagreements, even if it were possible.

A number of observations concerning Friedel-Crafts type catalysts need to be accommodated by any proposed mechanism. Pure anhydrous aluminum halides do not isomerize paraffins at mild conditions without the addition of hydrogen halides or of alkyl halides or water, both of which liberate hydrogen halides. Even with hydrogen halide present, trace quantities of promoters such as olefins, oxygen, bromine, or chlorine have to be added in some cases to initiate the reaction. At higher temperatures, promoters are unnecessary because olefins are generated by cracking. The cracking which accompanies isomerization at more severe conditions is suppressed by hydrogen, naphthenes, or aromatics.

All of these observations can be rationalized by a carbonium ion chain mechanism [28], illustrated in Table 5 for the case of butane. The initiating step is not so clearly defined, and Table 6 shows some of the possibilities. An olefin (present as a trace impurity or formed from an alcohol, an alkyl halide, or the interaction of a hydrocarbon with oxygen) can add a proton to yield a carbonium ion, thus explaining the need for a protonic source such as hydrogen halide or water. In the absence of any other source, the protonic catalyst might produce a carbonium ion by hydride abstraction. Such a mechanism permits rationalizing isomerization reactions in terms of the known behavior of carbonium ions. It explains the inhibiting effect of hydrogen and higher paraffins and the preferential hydrocracking of higher paraffins.

TABLE 5 Mechanism for Isomerization over Friedel-Crafts Catalysts

Isomerization of paraffins at the high temperatures required by "second generation" hydroisomerization catalysts is thought to follow a somewhat different mechanism [2931], as shown in Table 7. Here the initiating carbonium ions are generated via dehydrogenation over the platinum sites. The termination reaction no longer involves exchange with a feedstock hydrocarbon, but consists essentially of reaction with hydrogen. This is no longer a chain reaction.

The essential role of each of the two functions (acid and metal) has been strikingly demonstrated by the use of mixed powders of silica-alumina and platinum-charcoal for paraffin isomerization [32, 33]. Isomerization also occurs on a pure platinum surface, but the rates are slow compared with those of dual-functional catalysts, so the contribution of this route is probably minor.

It is believed that still another mechanism is operative in the case of the low-temperature (200-400°F) "third generation" hydroisomerization catalysts. The metal-catalyzed dehydrogenation would be severely rate-limiting, and the initiation step is probably similar to that proposed for Friedel-Crafts catalysts. The termination step involves the addition of hydrogen, and the overall scheme shown in Table 8 is, therefore, not a chain mechanism.

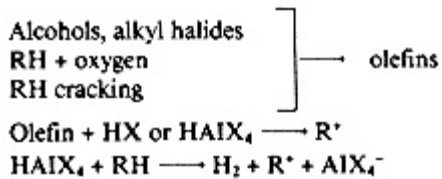
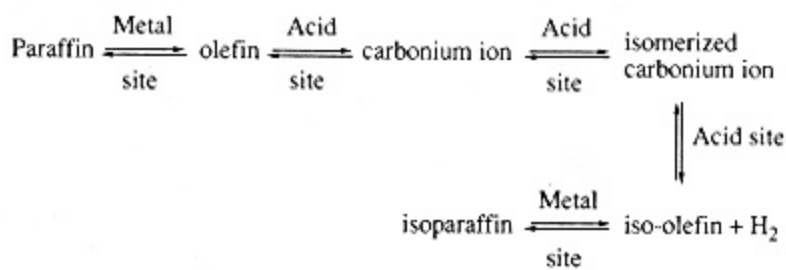
TABLE 6 Initiation Step in Isomerization

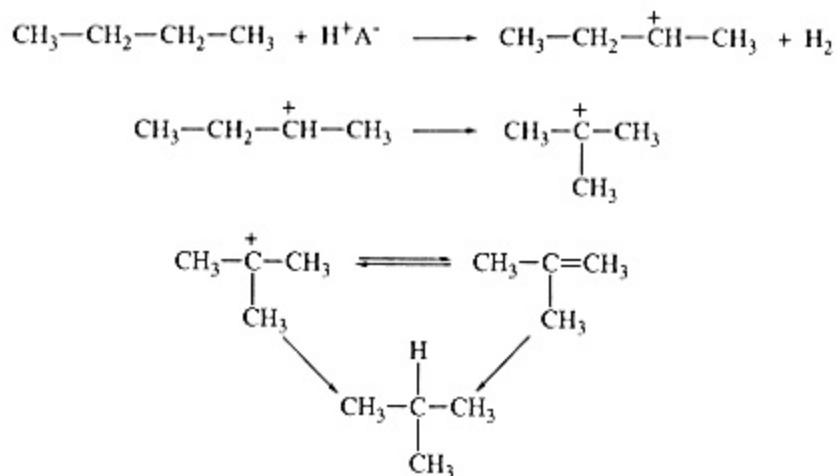
TABLE 7 Mechanism for Isomerization over "Second Generation" Catalysts

Process Flow Schemes

Processes based on low-temperature "third generation" hydroisomerization catalysts or on the somewhat higher temperature zeolitic catalysts dominate current commercial use and only these are discussed here.

Exact operating conditions are rarely published for processes offered for license, and the processes operate satisfactorily within a reasonably wide range of conditions. The following table gives an example of the ranges that typically apply to the more important light paraffin isomerization process variables:

Reactor temperature	250-550°F
Liquid hourly space velocity	14 h ⁻¹
Hydrogen-to-hydrocarbon ratio	14 mol/mol
Pressure	250-500 lb/in. ² gauge

TABLE 8 Mechanism for Isomerization over "Third Generation" Catalysts

The process flow diagram is basically similar for all processes. Figure 7 applies specifically to a C₅/C₆ unit using a low-temperature catalyst. Dry feed and makeup hydrogen (typically from a catalytic reformer) are combined with an organic chloride promoter, passed through appropriate heat exchange, and then proceed into the first of two reactors. The lead reactor is operated at a higher temperature to benefit from a fast reaction rate, and the second reactor at a lower temperature to take advantage of a more favorable equilibrium. The two-reactor setup is not essential, and some units have been built with only one reactor. The second reactor effluent is heat exchanged and cooled to condense the product, which is then stabilized for removal of dissolved hydrogen and light hydrocarbons formed by hydrocracking or contained in the makeup hydrogen. The organic chloride promoter, which is added in only parts-per-million amounts, is completely decomposed to HCl and leaves after neutralization by way of the stabilizer gas. Despite the presence of HCl, plants are constructed of carbon steel because the unit is kept dry.

Product C₅+ octanes of 8385 RON are typical for once-through operation with low temperature catalyst. Table 9 shows a typical product composition for this catalyst system. Higher C₅ content increases the product octane, as shown in Fig. 8. For butane isomerization, the same catalyst yields a reactor product containing around 60% by volume of isobutane. Product compositions for a typical operation are given in Table 10.

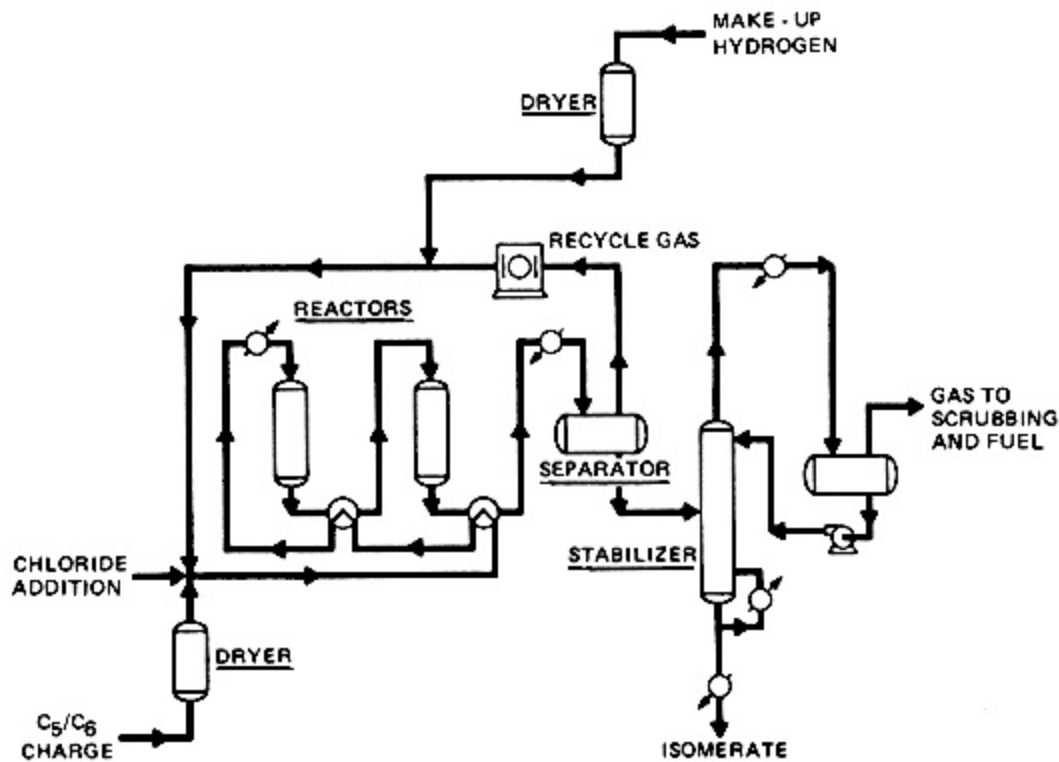


Fig. 7.
Typical isomerization unit.

TABLE 9 Low-Temperature Naphtha Isomerization Yields

Barrels per Day	Feed	Once-through Product ^a	Recycle Isomerization ^b
C1, SCF/d		31,100	35,800
C2, SCF/d		31,700	36,600
C3, SCF/d		178,800	195,000
i-C4		66	69
n-C4		23	25
i-C5	920	1,913	2,358
n-C5	1,435	474	30
Cyclo-C5	55	39	38
2,2-Di-Me-C4	20	887	969
2,3-Di-Me-C4	45	226	247
2-Me-C5	575	622	678
3-Me-C5	495	341	371
n-C6	1,080	207	12
Me-Cyclo-C5	170	79	78
Cyclo-C6	65	76	75
Bz	40		
C7+	100	20	20
Total C4+	5,000	4,973	4,790
Chemical H ₂ consumption, SCF/d		677,800	654,200
C4 Properties:			
RON	66.0	84.9	90.0
MON	64.8	83.1	87.9
Specific gravity	0.6550	0.6460	0.6451
RVP, lb/in. ² abs	11.5	14.8	15.4

^aUOP Penex Process.

^bUOP Penex and Molex Processes.

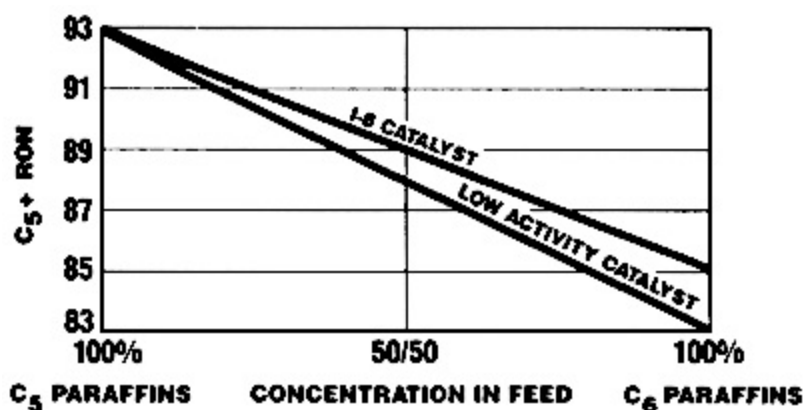


Fig. 8.
Normal paraffin recycle, octane vs feed composition. Basis:
C₅/C₆ paraffin feed.

TABLE 10 Typical Butane Isomerization Yields^a

Barrels per Day	Feed	Once-through Product
C1, SCF/d		35,500
C2, SCF/d		27,000
C3	1	1
i-C4	37	3,028
n-C4	4,940	2,027
i-C5	20	12
n-C5	2	8
Total, C3+	5,000	5,076
Chemical H ₂ consumption, SCF/d		47,800

^aUOP Butamer Process.

Zeolitic catalysts employ a similar flow configuration. The two-reactor system is less advantageous to these catalysts, however, since the equilibrium curve is less steep at the higher operating temperatures required. There is little octane advantage to be gained by intercooling, and a single reactor is normally used. Although the zeolitic catalysts yield a lower octane product than the low temperature systems, their rugged nature gives them some advantages. In general they are not sensitive to water and, since chloride injection is not used, feed driers are not required. Also, these catalysts are less sensitive to sulfur. In particular, some zeolitic types are able to maintain a high degree of activity on a continuous basis with sulfur levels in excess of 150 ppm. Based on a sulfur-free feed, once-through product C₅+ octanes from a zeolite catalyst system are in the region of 7981 RON. This octane will decrease somewhat as feed sulfur content is increased.

Higher Conversion Schemes

In once-through flow schemes the conversion of paraffins is limited by thermodynamic equilibrium. In some cases, however, it may be necessary to increase the amount of conversion. This is normally done by removing iso components from the feed or by separating and recycling the unconverted components from the reactor effluent.

C4 Isomerization with Recycle

The overall process flow scheme for butane isomerization depends on the specific application. Feed streams containing about 30% or more i-C₄ are advantageously enriched in n-C₄ by charging the total feed to a deisobutanizer column. A normal butane concentrate, recovered as a deisobutanizer sidecut, is directed to the reactor section as shown in Fig. 9. Feeds already

n-C₄-rich are charged directly to the reactor section. The n-C₄-rich feed is combined with recycle and makeup hydrogen, heated, and charged to the isomerization reactor. Reactor effluent is condensed and cooled, and flows to a separator where recycle hydrogen is recovered. Separator liquid is pressured to a stabilizer for removal of the small amount of light gas coproduct.

Stabilizer bottoms are returned to the deisobutanizer for recovery of an isobutane concentrate, per Fig. 9. Unconverted normal butane is recycled to the isomerization reactor section as a deisobutanizer side-cut. The system is purged of pentane and heavier hydrocarbons, which may be present in the feed, by withdrawing a small drag stream from the deisobutanizer bottoms. A typical deisobutanizer/butane isomerization material balance is shown in Table 11.

A separate deisobutanizer may be avoided by incorporating a butane isomerization unit into the design of new alkylation plants or into the operation of existing alkylation units. For this type of application, the capabilities of the isobutane fractionation facilities in the alkylation unit may be utilized to prepare a suitable high normal content isomerization unit feed and to recover unconverted normal butane for recycle.

C₅/C₆ Isomerization with Prefractionation

Fractionation may be applied in C₅/C₆ isomerization to increase product octane. Figure 10 illustrates the simplest application of this concept. Isopentane is removed from the isomerization unit feed by fractionation, resulting in a net increase in product isopentane content and decreased isomerization unit size. The isomerization reactor section is as in Fig. 7.

Economically, this option becomes attractive only when the feed isopentane concentration reaches about 30%. At this feed isopentane level, a deisopentanizer can increase total product octane about 2 RON above once-

TABLE 11 Typical Deisobutanizer/Butane Isomerization Yields^a

	Feed, BPD	Stabilizer Overheads, SCF/d	Deisobutanizer	
			Overheads, BPD	Bottoms, BPD
C1		52,700		
C2		40,000		
C3	30	42,000	30	
i-C ₄	1,493	23,500	4,828	1
n-C ₄	3,389		69	58
i-C ₅	67			34
n-C ₅	21			37
Total	5,000	158,200	4,927	130
Chemical H ₂ consumption, SCFB			75,000	

^aUOP Butamer Process.

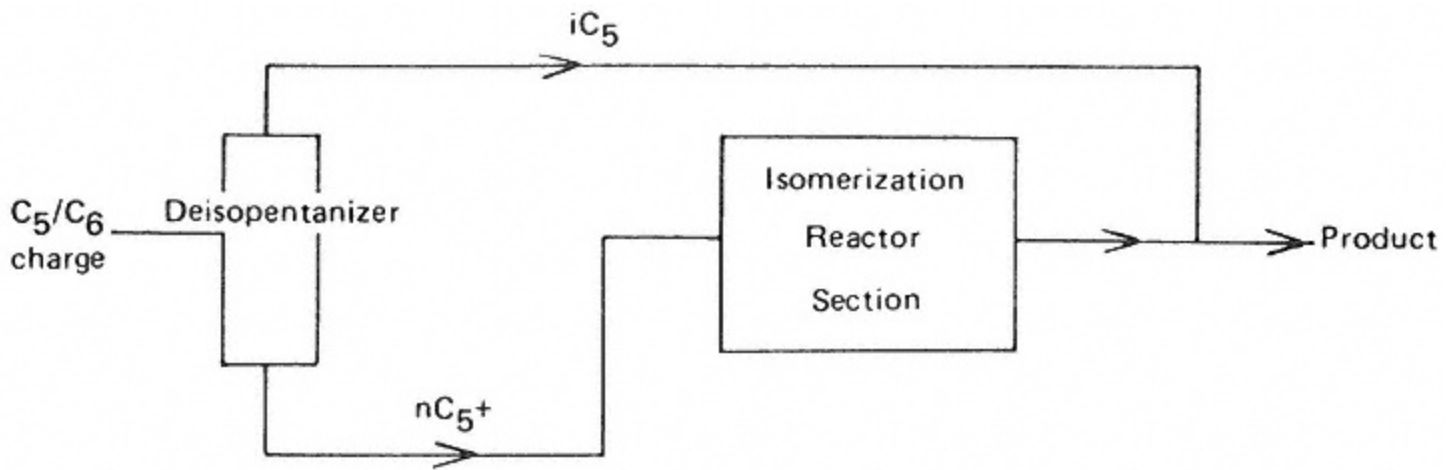


Fig. 10.
C5/C6 isomerization with prefractionation.

through isomerization. Below 30% isopentane content the deisopentanizer option is generally not economic.

C5/C6 Isomerization with Deisohexanizer Recycle

It is possible to achieve product octanes in the range of 8790 RON clear by using a single fractionator to recycle some of the lower octane components. With a deisohexanizer column, a split can be made between the higher octane dimethylbutanes and the lower octane methylpentanes. The dimethylbutanes and lower boiling components are then taken overhead from the column and separated from the methylpentanes and normal hexane, which are recycled to the reactors.

Figure 11 illustrates light naphtha isomerization in combination with a deisohexanizer column. This scheme is the simplest and one of the least expensive of all commercially available recycle isomerization schemes.

The high-octane product from this scheme is the overhead liquid from the column. The two other streams are a side-cut, which is recycled to the isomerization reactors, and a small bottoms drag stream, which allows C7 and cyclic components to be withdrawn from the system. The drag stream is of lower octane than the product and is normally sent either to a catalytic reformer or included with the product.

The deisohexanizer column needs only low-pressure steam for reboiling, and this scheme becomes especially attractive when there is an excess of refinery low-pressure steam. Although the energy consumption is higher than for recycle schemes using sieve separation, the investment requirements are considerably lower.

In C5/C6 isomerization, separating the low octane isomers for recycle may also be performed by using molecular sieves as shown in Fig. 12. Commercially, two major process alternatives are used for molecular sieve separation: one is a liquid-phase process and the other is a vapor-phase process. In both processes isoparaffins are separated out of the isomerate by taking advantage of the shape selectivity of the sieve

toward normal paraffins. The processes, however, differ substantially in equipment requirements.

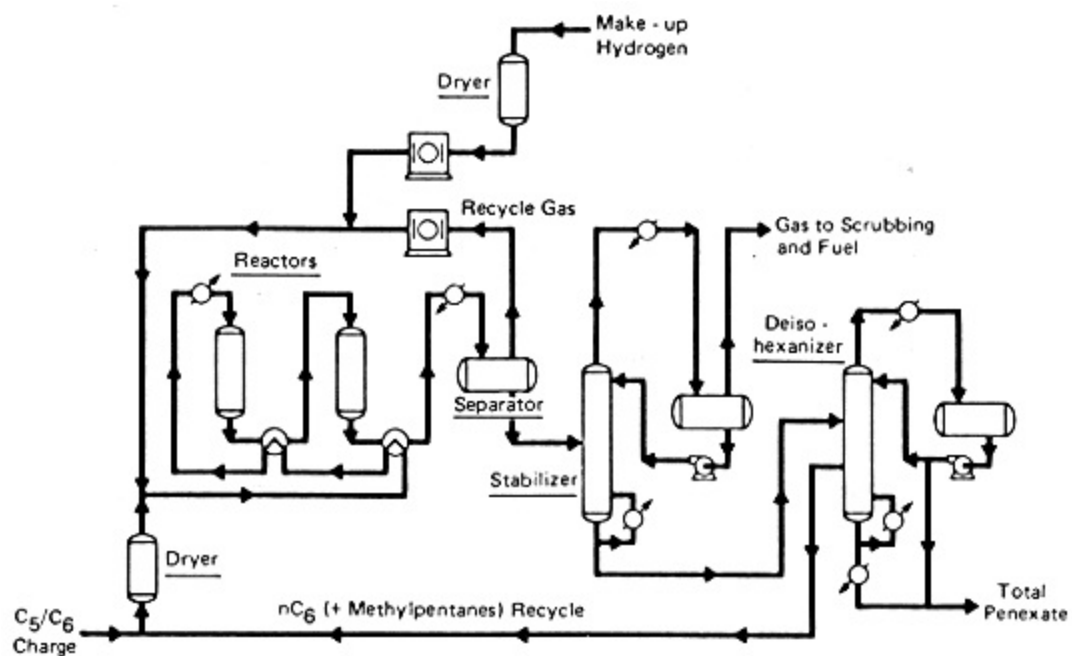


Fig. 11.
Isomerization with deisohexanizer recycle.

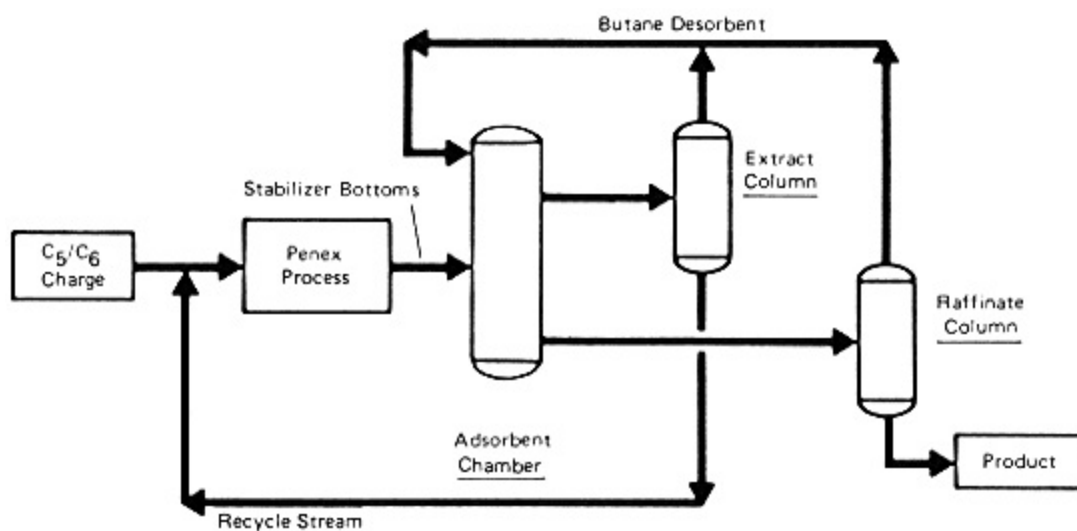


Fig. 12.
Isomerization/adsorption (liquid phase).

As with once-through schemes, the activity of the catalyst is also important to recycle schemes in determining the final product octane. Low-temperature catalysts produce especially high concentrations of the higher octane dimethylbutane isomers. The zeolite systems produce lower concentrations of these isomers. Since the sieve separation section is designed to recover normal paraffins, recycling does not compensate for the lower dimethylbutane content of the zeolite catalyst product. This results in a debit of between 0.5 to 1.5 octane numbers for the zeolite recycle system. Table 9 shows a typical product yield for a recycle system using low temperature catalyst and sieve separation.

For recycle systems processing a typical light straight-run naphtha, the fresh feed is sent to the isomerization unit. However, for light reformate feeds which contain appreciable amounts of benzene and olefins, or for feeds containing low proportions of normal paraffins, it may be desirable to combine this stream with the stabilizer bottoms from the isomerization unit and send it first to an adsorptive separation unit. This prevents the high-octane benzene from being hydrogenated to lower octane cyclohexane; it may also substantially reduce the quantity of heptanes that, when included in the isomerization unit feed, tend to hydrocrack to LPG.

Adsorption yields higher octane product when applied to pentane-rich isomerization feeds, as shown in Fig. 13. Feedstocks high in C₆ content benefit more from the deisohexanizer scheme in terms of product octane, because almost all of the C₆ paraffins are converted to high-octane dimethylbutanes. As in once-through processing, the low-temperature catalyst is very attractive in this recycle scheme because of its high selectivity to the dimethylbutane isomers.

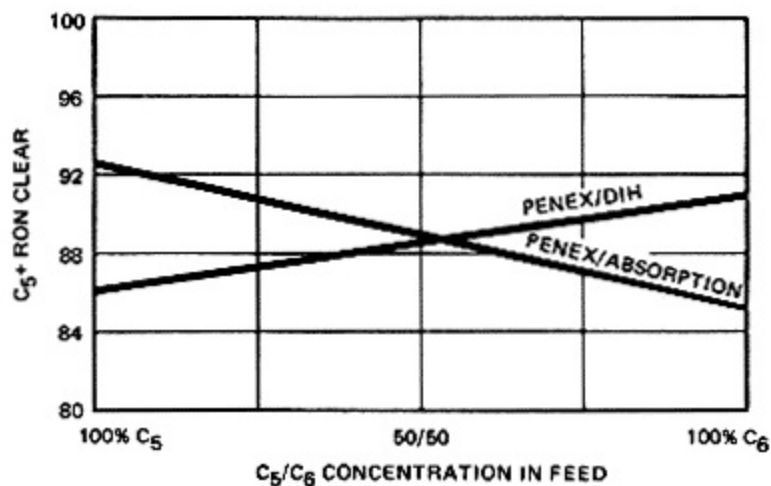


Fig. 13.
Product octane vs feed composition (paraffins only).

TABLE 12 Estimated Operating Requirements and Investment Costs
(Basis: 5000 BPD fresh feed)

	Butane		Naphtha	
	Once-through Isomerizationa	DIB + Isomerization	Once-through Isomerizationb	Recycle Isomerizationc
Operating requirements:				
Power, kW	121	168	265	416
LP steam, Mlb/h	7.7	21.8		15.9
MP steam, Mlb/h			8.1	9.7
Fuel fired, MMBtu/h	8.8	8.8		
Cooling water, gal/min	160	620	390	710
Catalyst and chemicals, \$/d	410	530	410	655
Operators	1.5	1.5	1.5	2.5
Estimated investment costs:				
Estimated erected cost, \$MMd	4.80	8.15	4.80	10.50
Catalyst and chemicals, \$MM	0.35	0.45	0.71	1.33

aUOP Butamer Process.

bUOP Penex Process.

cUOP Penex and Molex Processes.

dBasis: 1. U.S. Gulf Coast using modular construction, 1986.

2. Exclusive of offsites.

3. Includes stabilizer.

Operating Requirements/Investment

A summary of typical commercial light paraffin isomerization operating requirements is presented in Table 12.

Commercial Information

Industry acceptance of the light paraffin isomerization processes has been widespread. At the time of writing, over 60 light naphtha units have been commissioned and 9 others are in engineering design or construction. Nearly 40 C₄ isomerization units have been commissioned.

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Laser-Assisted Chemical Processing

Henry A. McGee, Jr.

The laser is now a commonplace tool on the factory floor as it is also commonplace in the medical operating room and in scientific instrumentation. Industrial applications center upon material processing. Here one is optically manipulating a beam of infrared light which allows welding or drilling or cutting applications in any normal situation as well as in inert or sterile environments. The beam can be focused to micron-size to allow work nearby to heat sensitive matter. The beam can be optically manipulated to reach into difficult geometries. Machining operations can be optically positioned to within high accuracies. These special characteristics offset the additional costs, and they make laser material processing economically viable.

Chemical processing applications are technically much more complex than is material processing or even medical applications where in both areas the laser is merely a sophisticated source of heat. Chemical processing applications are rarely pyrolyses alone, but rather they take advantage of the monochromaticity of the energy to affect species-specific excitations. Laser radiation is high fluence (J/s m^2), monochromatic, and coherent. Chemical processing applications utilize the first two characteristics. Coherency has not been important.

Laser-assisted chemical processing has occurred in separations and in denaturations, in the initiation of free radical chain reactions, in catalysis, in surface chemistry, and in the initiation of gas-phase reactions to produce solid films or fine particles. Laser radiation is expensive, so the value of the product or the enhanced efficiency of the process must offset these additional costs. Laser-assisted processing is new, and the examples discussed herein must, in general, be read for their suggestive power rather than as economically sound practically existing processes.

The laser and the process are, of necessity, intimately intertwined. So before reviewing processing applications, it is necessary to note some fundamental characteristics of the laser as a device and, in particular, those very few devices among a very large number that offer promise for practical application.

Fundamentals

A mole of molecules, 10^{23} of them, will arrange themselves among the available energy states in a Boltzmann distribution. The available energy states are fixed, they are determined by nature, and arise from electronic, vibrational, rotational, and translational motions of the molecule. The mechanism that drives this distribution is simple chance, and when the molecules

are so arranged, the mole of matter is said to be at thermodynamic equilibrium.

To produce a laser, we must arrange to invert this thermodynamic distribution. The laser is a nonthermodynamic device, and its value in chemical processing is typically also nonthermodynamic. Coupling or energy transfer between the four types of molecular energies occurs in finite time, and it is frequently slower than is the transfer among the energy states of a particular one of the modes. It is possible to invert, for example, a vibrational population without destroying the Boltzmannian translational distribution. Or one can invert an electronic distribution without destroying the Boltzmannian vibrational distribution. Or any sort of combination and extent of inversion may be produced. However it may be produced, the population inversion and its separation from the remaining energy modes is transitory, for relaxation back to a state of thermodynamic equilibrium occurs at rates depending on the modes and the specific molecules that are involved. A fast energy input is necessary to produce the desired inversion, and this process is referred to as "pumping the laser." Electric discharges, photolyses, and chemical reactions have all been employed as pumping processes. Even a fast nuclear fission reaction, an atomic bomb, has been proposed as a means to pump a high energy X-ray laser.

Suppose the population inversion has been made to occur in a material held between two mirrors as schematically depicted in Fig. 1. Such a configuration is called an optical cavity.

Some of the excited species will spontaneously emit a photon, again at a rate determined by nature, and some of these will be intercepted by the mirrors at either end of the optical cavity and be reflected back down through the material toward the opposite mirror. When a photon of energy, $h\nu$, encounters an energetic species that is exactly $h\nu$ above a lower energy level, a stimulated emission may occur, again at a rate given by nature. So a photon collides with an energetic species to produce two photons of exactly the same energy and a lower energy species. This stimulated emission produces a cascade of photons throughout the cavity as the photons are reflected back and forth by the two end-mirrors to provide a high number density of photons. One mirror may have a hole in it or be partially transmissive to

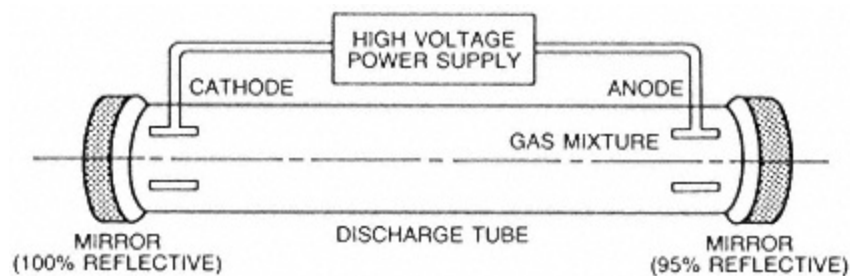


Fig. 1.
Schematic of a typical gas laser configuration.

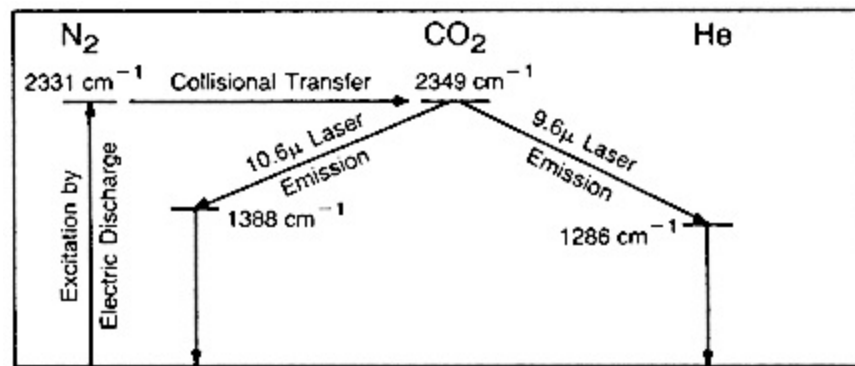


Fig. 2.

Energy diagram for CO₂ laser action showing effect of N₂ and He.

allow a portion of the cascade to escape to produce a laser beam. The word laser is an acronym for light amplification by stimulated emission of radiation. The power of the beam in watts will depend upon the number density of excited states, the rate of stimulated emission, and the energy of the transition. The laser fluence is measured in W/m² or J/s m².

The most common device in practical use is the CO₂ laser which is depicted on a vibrational energy diagram in Fig. 2.

An electric discharge is conducted in a mixture of He, N₂, and CO₂. The N₂ is excited by the discharge and transfers its energy to the CO₂. The CO₂ lases near 10 μm into a lower energy state that is in turn efficiently depopulated by collisions with He. If it were not for the helium, the concentration of the lower energy CO₂ would build up to produce upper and lower states populated in a Boltzmann ratio, at which time laser action would cease. That is, $n(\text{lower state})$ must be kept less than that given by $n(\text{lower state}) = n(\text{upper state}) \exp [-(\epsilon_{\text{upper}} - \epsilon_{\text{lower}})/kT]$.

Practical Lasers

The family of laser devices that may be ascribed to be practically useful is time and situation dependent. The energy out in the beam is less than the energy used to pump the population inversion. For the CO₂ laser this wall-plug efficiency is about 10%, so laser photons are inherently expensive. In addition, the utilization of the laser photons in some chemical processing task will always occur with less than unit efficiency. The proposed processing application must offer some economically attractive characteristic to offset these large economic detractors.

With the value of the sorts of chemical reactions and processes now existing or imagined, only the CO₂ laser, one of the excimer lasers, or the Nd:YAG laser has seen engineering development to the point of potential real utility. Laboratory and industrial scale devices are available from a number of manufacturers in the United States and in Europe.

The CO₂ device is pumped by an electric discharge, it involves innocuous and inexpensive chemicals, maintenance and safety matters are routine, and it is a common device on the factory floor. It produces dozens of useful lines in the infrared region between 9.5 and 10.5 μm . Many molecules exhibit vibrational absorptions in this region, and each represents a convenient potential receptor. CO₂ devices that produce gigawatt pulses have been built for studies in thermonuclear fusion.

TABLE 1 Characteristics of Excimer Lasers

Laser	Wavelength (nm)	Energy (kcal/mol)
ArF	193	148
KrCl	222	129
KrF	249	115
XeCl	308	93
XeF	350	82

The excimer devices are a family of lasers with energies as summarized in Table 1. They are pumped by an electric discharge, and they require expensive and corrosive chemicals (noble gases and fluorine). Many molecules exhibit broad absorptions in their electronic energy levels at these ultraviolet frequencies, and each is again a potential receptor.

Solid yttrium-aluminum-garnet may be doped with neodymium ions (the Nd:YAG). A rod of this solid solution of Nd³⁺ may be flash photolyzed by an array of Xe lamps to produce electronically excited ions. The energy pools in an excited $4F_{3/2}$ state with a long lifetime of about 900 μs and from which laser action occurs at 1.06 μm . High power laser pulses can be produced from this device, for the number density of ions in the optical cavity, i.e., in the solid rod, can be made high. These giant pulses cannot, however, be produced at high rep rates because the rod is heated by the pumping flash, and it can only be cooled by slow thermal conduction.

The above family of practically useful lines can be somewhat expanded. For example, the Nd:YAG may be frequency doubled with efficiencies as shown here:

Wavelength (nm)	Relative energy output
1064	1
532	0.4
266	0.1

In addition, Raman shifting of lines occurs with high energy efficiency. For example, the 350-nm line from XeF can be efficiently shifted to 585 nm with barium vapor.

There are dozens of other systems that have been made to lase. None offers the technical promise of the devices noted above.

The Chemical Laser

Although it is irrelevant as an aid in chemical processing, the chemically pumped laser should be noted, for it, as a device, is an exercise in chemical process engineering albeit in an unusual sense. In some exothermic reactions, like that between F and H₂,



the exothermicity initially appears as vibrational excitation of the product HF. An inversion is chemically produced, and lasing occurs over lines near 2.7 μm . One way to build such a device is as a gas dynamic laser, which appears schematically in Fig. 3. Here fluorine atoms are produced by dissociation of the molecule by collision with hot nitrogen from an electric arc. The F atoms in the inert carrier gas expand to supersonic velocities through a line of nozzles whereupon hydrogen is injected into the exit stream. To design such a device, one has all of the problems of simultaneous fluid flow, chemical reaction, and diffusion (see Fig. 4). This is a chemical reactor from which the product is a beam of energy rather than some chemical species. The vibrationally hot HF's are stimulated down in the optical cavity formed by the two

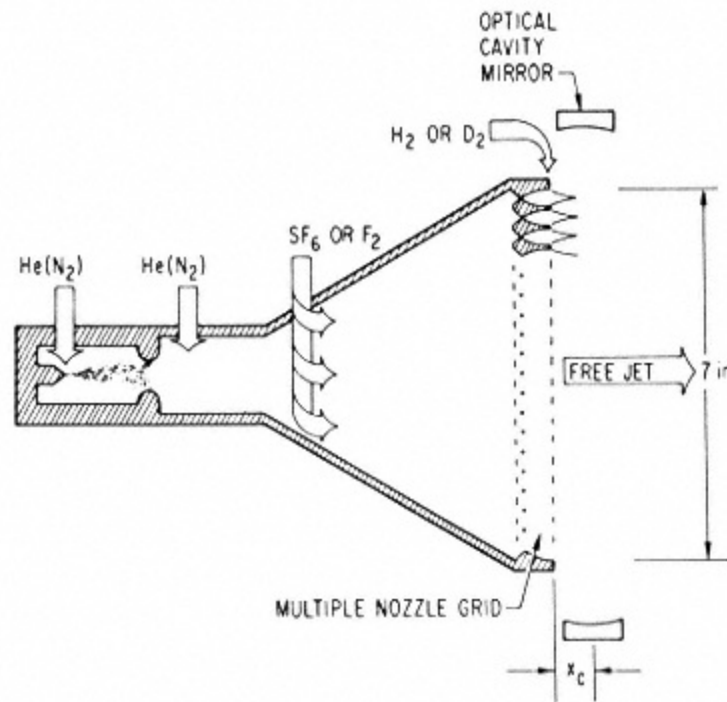


Fig. 3.
Gas dynamic laser pumped by the reaction $\text{F} + \text{H}_2 \rightleftharpoons \text{HF}^* + \text{H}$.
(Used with permission of Wiley-Interscience.)

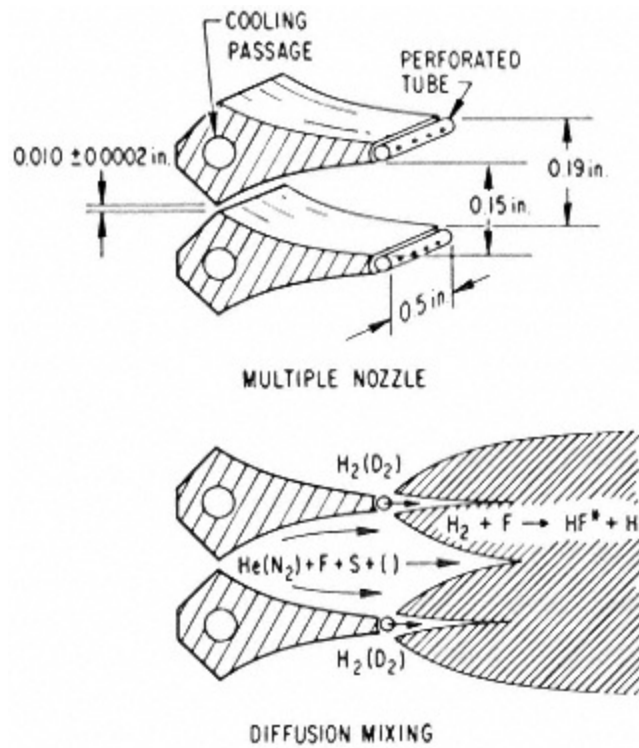


Fig. 4.
Gas dynamic laser showing supersonic diffusive mixing and
reaction of H_2 and F to produce vibrationally excited HF^* .
This laser emits at $2.7 \mu m$.
(Used with permission of Wiley-Interscience.)

opposing mirrors, and the supersonic flow continuously brings hot molecules into the cavity and carries out equilibrium molecules. This hydrogen-fluorine chemistry is the basis of a large strategic defense system called ALPHA that would operate with output power levels of 5 to 25 MW.

Many chemical lasers are known [1], each involves chemical process engineering in essential ways, but none will likely be useful in laser-assisted processing.

Mechanistic Considerations

Multiphoton Absorption

Photons from one of the excimers or from Nd:YAG have wavelengths between 193 nm and $1.06 \mu m$ or have energies between 148 and 27 kcal/mol. These are of a size to overcome typical activation energies in chemical processing. But CO_2 photons at $10 \mu m$ have only 2.86 kcal/mol. In addition, resonant vibrational absorption would seemingly be spoiled due to anharmonicity of the vibration. Yet 20 to 30 photons may be readily absorbed. This occurs because overtone and combination levels and rotational lines act

together to create a high density of states above the first two or three vibrational levels. These initial frequencies are, to a good approximation, harmonic, and absorb at a single fixed frequency. Radiation at this single frequency will push the molecule up the one or two equally spaced levels into the high density region which will then continue to absorb that single frequency again and again. This high density region is referred to as a quasicontinuum. The absorption of CO₂ radiation in



requires that *n* be approximately 35. Obviously multiphoton absorption has occurred, and all at a single forcing frequency. SF₅Cl can be similarly excited. The strong SF bonds absorb CO₂ radiation; the weak SCl bond does not absorb, but it is the bond that is broken due to intramolecular migration of the energy.

The requirement of little anharmonicity at the lower levels and a high density of levels in the quasi-continuum is satisfied by all polyatomic molecules containing at least three atoms other than hydrogen.

Pressure Dependence

Intermolecular collisions and resulting energy transfer degrade any species-specific or mode-specific excitation that may have been induced by laser radiation. Such collisional degradation is reduced by operating at low pressures, but at the expense of then lower mass throughputs. The required low pressures have very negative implications as regards practical utility.

An interesting demonstration of the significance of pressure and thus collisional energy transfer is evident from the irradiation of mixtures of ethyl acetate and isopropyl bromide from a CO₂ laser [3]. The ester absorbs, but the halide does not. At 20 torr the production of ethane from the ester and propene from the halide agreed with simple thermal data, suggesting that the laser is serving as a sophisticated Bunsen burner. At lower pressures, however, ethane was dominant, showing that the energy placed in the ester stayed there to produce reaction and was not collisionally transferred to the halide. This sort of selectivity is pressure dependent and/or power dependent. For power dependency, getting faster energy input can produce reaction before relaxation into other species that may also be present can occur. The photolysis of alkyl halides in helium with propylene also present using CO₂ laser radiation revealed propylene decomposition even though the olefin is much more stable than the halide [4]. Again, a nonthermal process has occurred.

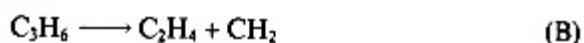
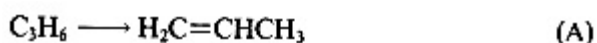
Laser-Stimulated Chemical Reactions

Bond-Specific Photochemistry

Bond-specific photochemistry is an illusive but highly sought goal of laser-stimulated reactions. To be sure, a specific functionality of a molecule can be specifically excited using the monochromaticity of the laser. The energy

necessary for reaction may then be deposited exactly where it is needed. The problem arises when this specific excitation migrates into the remainder of the molecule at rates generally greater than the chemical reaction rate at that excited functionality. This problem may be overcome, in principle, by delivering the energy in a very short time, say picoseconds, with sufficient intensity to cause bond breakage or whatever phenomenon that is desired at that site faster than the energy may be shared within the molecule. Another way to reduce thermalization utilizes an absorbing functionality in a molecule in which intramolecular energy transfer is slow, but this will be a highly specific situation.

The illusive true bond specific photochemical reaction may have occurred in the unimolecular decomposition of cyclopropane [2]. Two channels are evident:



where (A) and (B) have activation energies of 65 and 100 kcal/mol, respectively.

Excitation of the CH stretch at 3106 cm^{-1} favored the lower energy isomerization, implying randomization of the energy. Excitation of the CH_2 wag at 1080 cm^{-1} of the cyclopropane, however, produced more decomposition. Depending upon the mode that is excited, it would appear that the excitation is nonstatistical or that it is mode-selective in some sense.

Chain Reactions

Initiation of chain reactions from laser irradiation are the most promising from a practical perspective, for here many product species are formed for each free radical that is initially produced by the laser. That is, high quantum efficiencies are evident, and many product molecules are produced per expensive photon that is absorbed. Radical reactions typically require perhaps twice as much as energy to initiate as to propagate. By its nonthermodynamic character, the laser can produce free radical initiators at much lower temperatures than are required for thermal initiation. This operation of the reactor at lower temperatures both improves product stability as well as freezes out undesired side reactions which represent inefficiencies in feedstock conversion as well as presenting problems in downstream processing for the removal of these undesired by-products. The species specificity of the laser means that only the radical initiator is attacked by the photolysis. The generation of these initiators occurs in the bulk of the reactor stream far removed from hot walls that must be present in the purely thermal reaction. These heated surfaces frequently cause undesirable catalytic effects on the chemistry.

Vinyl chloride monomer for the production of polyvinyl fluoride can be produced from dichloroethane at rates as high as 10^4 product molecules per photon. The conventional process operates near 500°C and 10 atm with 60%

conversion and with the production of undesired side-products. The yield was increased to 7080% conversion using XeCl laser irradiation at 308 nm. Upon lowering the temperature to 150°C, the yield was at the original 60%, but now with a selectivity of 99.9% [5].

Another chain reaction that illustrates the power and the problems of laser initiation is the production of cumene hydroperoxide from cumene in the presence of oxygen. Using the XeF laser at 350 nm, the quantum yield is 500 at 120°C. The peroxide is useful but fragile. The laser allows operations at lower temperatures than would otherwise be possible, and therefore allows greater product stability.

Laser-Assisted Catalysis

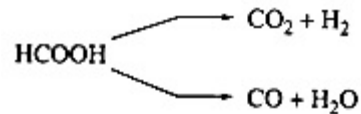
We will categorize as laser catalysis those processes in which the irradiation affects diffusion to or away from a catalytic surface, adsorption or desorption, as well as when it affects the mobility of an intermediate upon the catalytic surface. We will also classify as laser-assisted catalysis all those processes in which the catalytic moiety is generated in situ by laser irradiation.

An example of in situ catalytic generation is that of the irradiation of an olefin containing some COS. The COS strongly absorbs CO₂ photons. The cis to trans conversion of the olefin is catalyzed wherein the active catalyst appears to be S₂ which is produced from the laser-promoted dissociation of COS.

Another example wherein laser irradiation evidently produces the catalytic agent in situ involves the irradiation of one-pentene containing iron pentachloride, Fe(CO)₅ [18]. The carbonyl is evidently deligandized by the XeCl excimer laser radiation at 308 nm to produce Fe(CO)₃ which is the active catalyst. The conversion of 1-pentene is observed in both the liquid and gaseous phase. Several available lines may be used, but that from XeCl is interesting, for the hydrocarbon does not absorb at this energy. There is no reaction in the absence of light, and no reaction with light in the absence of Fe(CO)₅. At rep rates above about 4 Hz, quantum efficiency decreases, indicating the decomposition of intermediates during the irradiation. Below 4 Hz, this efficiency is constant, suggesting that the system relaxes between pulses. Thus one estimates the active catalyst lifetime at about 0.2 s. At the operating temperature of 70°C, thermally initiated catalysis is negligible, but with the laser, a minimum of 1000 catalytic cycles is observed for each photon that is absorbed. Laser irradiation may affect heterogeneous catalytic processes in a variety of ways. Reactants adsorbed on a catalytic surface may be assisted over the activation energy if radiation of proper frequency is absorbed by one of the reactants. The diffusion rate on a catalytic surface may be similarly enhanced by resonant and highly efficient absorption of energy from laser irradiation. Desorption rates of a product species may be enhanced. Even selective desorption of one isotopic species over another may occur because of the monochromaticity of the incident laser irradiation. Experiments are difficult due to both surface heating that would mask selective laser-induced processes as

well as problems in separating effects due to gas-phase and surface-phase contributions.

An example involves the effect on reaction pathway of irradiation of platinum as it catalyzed the decomposition of formic acid. Two pathways are evident,



When irradiated with the R(20) line at 9.6 μm from a CO_2 laser, the ratio of CO_2 to CO was enhanced by 50% with the change resulting from a decrease in the CO product [20]. Among all the possible phenomena perhaps caused by the radiation, there remains uncertainty as to the mechanism of this remarkable effect on the catalytic pathway of this simple reaction.

Isotope Separation

Isotopically enriched uranium is very valuable in small amounts, and the isotopes are difficult to separate by conventional schemes. These are all positive characteristics for possible laser processing, and in 1985 a laser-based process was selected by DOE from among several competing processes to go on to operations on a practical scale [6]. Laser-based separation is the technical method of choice, far surpassing the old gaseous diffusion process. The so-called AVLIS process, atomic vapor laser isotope separation, brings natural ^{235}U from 0.7% to about 3%, i.e., to reactor quality. AVLIS has undergone pilot-plant trials and operations for 13 h/d and 5 d/week have been achieved. Both operating costs and capital costs of the laser-based process are nominally 10% of these costs for competing gaseous diffusion or centrifuge processes.

AVLIS has seen the most extensive engineering development of any laser-based process. This also utilizes especially designed copper laser pumped dye lasers which violates our earlier assertion as to which devices offered practical utility. This violation is allowed by the unique character and value of the product, and it will not likely be a situation to be duplicated in other chemical processing operations. Here we arrange for low pressure uranium vapor to be irradiated with energy sufficient to ionize ^{235}U but not sufficient to ionize the 99.3% ^{238}U that is also present. A nearby negative plate completes the separation.

A two-step photodissociation process similar to AVLIS has been used to enrich ^{33}S [7]. Here combined KrF and CO_2 pulses produce the enrichment evident in Fig. 5. The enrichment, E , along the ordinate is the ratio $^{33}\text{S}/^{32}\text{S}$ in the SO_2 after irradiation to the same ratio before irradiation. Only the OC^{33}S is excited, and enriched SO_2 is evident from the reaction mechanism. But O atoms are also formed, and these react indiscriminately with OCS to spoil the specificity. A free radical scavenger such as NO_2 will preferentially react with these O atoms and enhance the specificity. The positive effect of decreasing pressure upon yield is again evident.

Isotope enrichment of a factor of 3 has been achieved by the selective

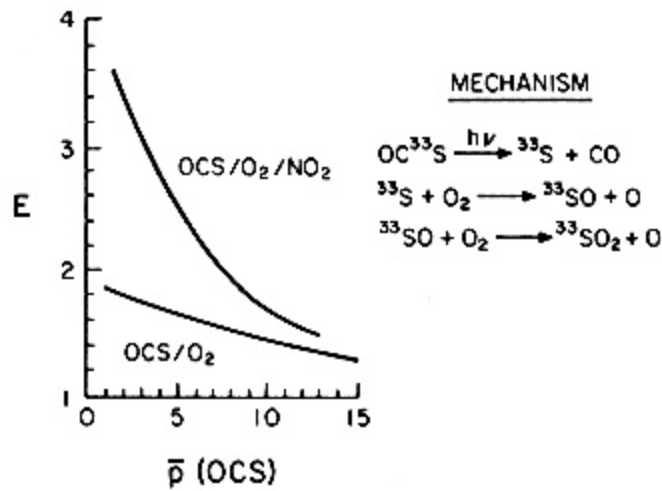


Fig. 5.
Enrichment of ^{33}S due to combined KrF and
CO₂ laser irradiation.

evaporation of $^{11}\text{BCl}_3$ from a frozen film of $^{11}\text{BCl}_3$ and $^{10}\text{BCl}_3$ on a transparent substrate at 77 K [8]. The film was irradiated from the reverse side through the substrate using a CO₂ laser. A similar scheme can be used to desorb HDO selectively from a film of HDO and H₂O on a transparent substrate [9]. Here OH absorbs at 2.62.8 μm while OD absorbs at 3.53.7 μm . As always, energy exchange from the initially excited HDO can thermalize the system and spoil specificity.

There are dozens of examples of isotope separation, but these three illustrate their character and their potential.

Purification and Denaturation

Impurities present in low concentrations have been efficiently removed by laser processes. These are efficient utilizations of laser photons, for the removal of a few undesired molecules greatly enhances the value of the many desirable molecules. Laser techniques process only the small contaminant, while conventional techniques process the entire stream.

Consider, for example, the removal of 1 ppm of H₂S from syngas which is important protection to enhance the useful life of Fischer-Tropsch catalysts. ArF excimer radiation at 193 nm dissociates H₂S to form HS that reacts with a nearby metal surface to produce either a nonvolatile sulfide or elemental sulfur [10]. The process has been patented. The absorption of the laser radiation by the H₂S is 10^7 times that of the syngas that is present in 10^6 greater concentration. Absorption of photons by C₂H₄ and CH₅OH, also present as impurities, is a nonproductive loss of photons, for these impurities do not poison the catalyst. The laser process attacks the one undesired molecule in 10^6 , while a charcoal adsorption, for example, demands that all 10^6 molecules be pumped through the bed.

Very pure silicon for the electronics industry may be made by reducing very pure silane. But SiH_4 typically contains AsH_3 and PH_3 as common impurities. These have been selectively attacked and precipitated using ArF laser irradiation [11]. AsH_3 and PH_3 , each at 50 ppm, were reduced to below gas chromatographic detection limits of less than 0.5 ppm. Enhanced efficiency occurs upon cooling from 295 to 198 K due to a decrease in the absorption cross-section of SiH_4 by about 35% upon cooling.

The common impurity phosgene, COCl_2 , may be removed from BCl_3 using CO_2 laser radiation [12]. COCl_2 does not absorb at $10\text{ }\mu\text{m}$. Rather the BCl_3 strongly absorbs at 956 cm^{-1} and efficiently transfers its energy to COCl_2 via a vibrational resonance in BCl_3 at 240 cm^{-1} and in COCl_2 at 243 cm^{-1} . The compound dissociates into CO and Cl_2 . The reaction is nonthermal, for the concentrations of products exceeded that from thermal dissociation at 500°C even though the laser-assisted reactor was never more than warm to the touch. This transfer mechanism was proven by experiments with mixtures of C_2H_4 , which also strongly absorbs CO_2 radiation, and COCl_2 . But here there is no vibrational resonance, and COCl_2 loss is weak. Compounds can be purified even though the impurity itself does not absorb.

There are many examples, but the character of a species-specific attack upon a species present in low concentration is evident.

Laser radiation may be used to selectively pump a cis to trans conversion, or the reverse, with little accompanying decomposition [13]. Reversal of the process to yield an equilibrium cis/trans mixture is recovered by merely heating the product mixture.

Other sorts of isomeric equilibria may be driven one way or the other. The fully fluorinated cyclobutene can be converted to the open chain di-olefin by CO_2 laser irradiation at $10.5\text{ }\mu\text{m}$ [19]. The cyclic isomer is 12 kcal/mol more stable than the open isomer. The activation energy for the ring-opening reaction is 47 kcal/mol while that for the reverse reaction is 35 kcal/mol. Therefore it is essential that the higher energy product be immediately quenched, for it possesses the activation energy to revert. This requirement for a rapid quench is accomplished by conducting the laser-driven process in a large excess of helium.

Liquid-Liquid Extraction

Although not completely convincing, laser-assisted liquid-liquid extraction is nonetheless compelling [14, 15]. The uranyl nitrate ion has been transferred from an aqueous phase by formation of a complex with tributylphosphate in an organic phase. The arrangement is shown schematically in Fig. 6. The ion absorbs at 945 cm^{-1} , and the ester groups of the complexing agent absorb at 1040 cm^{-1} . Both are selectively and independently excited by an appropriate line from the CO_2 laser. Radiation of the oil/water interface at 945 cm^{-1} doubles the equilibrium extraction, while radiation at 1040 cm^{-1} , where the complexing agent absorbs, is ineffective. Evidently the chemical potential at the interface has been changed. It may also be that the observed results may be the result of agitation at the

interface produced by the sudden deposition of heat from the absorbed laser radiation.

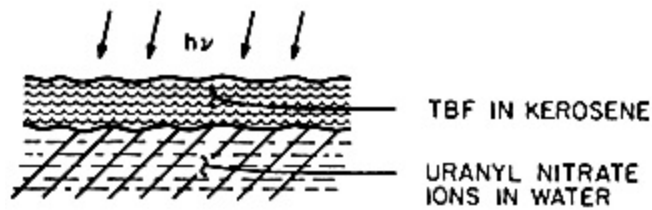


Fig. 6.
Laser-assisted liquid-liquid extraction.

Surface Reactions

In an electroplating arrangement, the beam from an argon ion laser passes through a gold-bearing electrolytic solution to illuminate the surface of an electrode at precise spots. Gold is deposited only at the illuminated spots [16]. The mechanism of action is unclear, for the surface may be cleaned or heated or the chemical potential may be otherwise modified. The rate of electrodeposition is enhanced. Gold may be conserved, for gold is here deposited only where it is required. The laser technique is more convenient than masking techniques when working with complex three-dimensional shapes.

Another example of laser-enhanced surface chemistry is evident in the production of diffraction gratings on gallium arsenide [17]. Here two beams constructively and destructively interfere to produce a series of alternating illuminated and dark stripes on the surface of the semiconductor. The plate is irradiated while immersed in an oxidizing solution, where only the illuminated surface oxidizes. The oxidized material dissolves into the solution, leaving a precisely etched or grooved surface.

Solids from Laser-Stimulated Gas-Phase Reactions

The laser pyrolysis of gases can produce small particles of uniform size that have attracted attention as catalysts and as feed materials for powder metallurgical techniques. Laser radiation from a CW CO₂ device has been directed onto either silane or silane/ammonia mixtures or silane/ethylene mixtures. These have produced metallic Si, Si₃N₄, and SiC, respectively [22]. One of the most interesting aspects of this technique is the production of spherical and nonagglomerating particles of narrow size distribution that can be effectively sintered and thus lead to ceramics of superior properties. The high temperature ceramic silicon nitride has attracted attention for use in machinery. These appear to form an ideal powder for subsequent sintering. Previous techniques produce powders that have large size distributions, that are nonspherical, and which agglomerate all of which lead to a poorly sintered and perhaps flawed final product. The success of the laser technique rests upon pyrolysis free of heterogeneous nucleation sites and wall contamination. Ammonia and silane were chosen as reactants, for both absorb near the 10- μ m band of the CO₂ laser. Optimum pressure was, however, again low at about 0.03 atm or about 25 torr.

The technique has already been used to produce "alloys" of metals which are conventionally immiscible, for example, iron and bismuth, by the radiation of suitable precursors [23]. This again portrays the ability of laser irradiation schemes to suspend the laws of thermodynamics momentarily and here produce a homogeneous mixture of immiscible metals.

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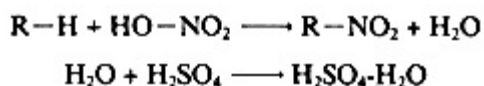
Nitration

Ernest O. Ohsol

Nitration is one of the classical unit processes of synthetic organic chemical manufacture. In all cases, a nitro group (NO_2) is introduced into an organic compound, usually to be attached directly to a carbon atom. In some cases, however, it is attached through an oxygen atom (in nitrate esters, such as nitroglycerine and nitrocellulose) or through a nitrogen atom (as in nitroguanidine, cyclonite, and tetryl).

Originally nitration was developed, at least in peacetime, as a process for making nitroaromatics such as nitrobenzene, nitrotoluene, nitrophenol, nitronaphthalene, and nitroanthracene, introducing one or more nitro groups onto ring carbons and, in most cases, carrying out further reactions such as reduction to amino groups and diazotization. These processes were developed for the dye, pharmaceutical, and photographic chemical industries.

The replacement of an aromatic hydrogen atom attached to a carbon by a nitro group is carried out with nitric acid, generally mixed with sulfuric acid, in accordance with the following equations:



The strength of the acids used depends upon the strength of the carbonhydrogen bond being attacked, a strong acid being used when the bond is tight. Various theories have been proposed to explain the mechanism of the reaction; one of the best accepted ones is that the active nitrating agent is nitronium nitrate, $\text{NO}_2\text{-NO}_3$, which dissociates to NO_2^+ and NO_3^- ions. The NO_2^+ ion is the active nitrating agent, displacing labile (potentially positively charged) hydrogen atom on the aromatic ring. Since $\text{NO}_2\text{-NO}_3$ or N_2O_5 is an anhydrous residue from two nitric acid molecules, the nitrating acid must be a water-accepting medium, i.e., containing strong sulfuric acid (or strong nitric acid). In some cases other water-binding media are used, for example, glacial acetic acid.

Interestingly, the presence of substituents on the aromatic ring may greatly influence the charge distribution around the ring. The so-called negative substituents such as OH (in phenol) generate a positive ring carbon next to the substituent, followed by a negative carbon in each ortho position, a positive carbon in each meta position, and again, a negative carbon in the para position.

The negative carbons then cause their attached hydrogens to be relatively positive, i.e., labile and easily substituted by a nitro group. On the other hand, positive substituents, such as a carboxy group, a sulfonic acid group, or a nitro group already in place, favor the attaching carbon to be negative, and the

ortho and para carbons then become positive, making the attached hydrogens more negative and less labile. The meta position would then be relatively more negative, with their hydrogen becoming the more positive (labile) ones. It may thus be said that certain substituents on the ring are ortho-para directing and others are meta directing. In general, the meta-directed substitutions are less reactive than the ortho-para ones.

Table 1 summarizes the situations.

When nitration has proceeded to a point where the acid strength has been reduced sufficiently by the water of reaction, nitration will slow down and eventually stop even though nitric acid remains in the mixture. However, if there is sufficiently strong sulfuric acid still present, essentially all the nitric acid may be consumed.

Nitric acid is also a strong oxidizing agent, and its activity on this score is not restricted to nitronium ion concentration, but rather to temperature and catalytic effects. For a good clean nitration, it is therefore desirable to limit the reaction temperature by cooling the reactor, relying on acid strength rather than temperature for achieving a desirable reaction rate. In cases where the substrate compound is very easily oxidizable, the vulnerable group, such as the amino group in aniline, may be "protected" by acetylation before nitration. The acetyl group may later be hydrolyzed off to give the desired nitroaniline product.

In the post-World War II period, nitration of the lower aliphatic compounds was commercialized to give the nitroparaffins and their derivatives. Methane, ethane, and particularly propane have been successfully nitrated on a large scale, directly. This reaction is completely different from the liquid phase mixed-acid nitration discussed above. Due to the lesser reactivity of the aliphatic carbonhydrogen bond, a higher temperature must be used, and prevention of oxidation (and explosion) is a major problem to be overcome. This process is discussed in a separate section.

Major nitration processes which may be considered as examples of liquid phase, mixed-acid nitrations are benzene and toluene nitrations where the substrate is an aromatic hydrocarbon, and glycerol nitration where the substrate is a hydroxy compound and the product is really an ester.

TABLE 1

Substituent Group	Directing Influence	Rate Effect
OH-	o-p	+
NH ₂ -	o-p	+
Alkyl	o-p	+
Cl, Br, or I-	o-p(more p)	-
SO ₃ H	m	-
COOH	m	-

Nitration of Benzene

Benzene is nitrated on a large scale to make mononitrobenzene, which is mostly used to make aniline by reduction. The process is generally conducted in large, well-agitated reactors with internal cooling at a temperature of 50–60°C. The reactors are generally made of alloy steel, with a propeller-type agitator set inside a sleeve so as to circulate the vessel contents through the sleeve, and down through either horizontal coils or vertical tubes mounted in a calandria.

For continuous nitrators, a strong fortifying acid is added at a point of high turbulence, and a corresponding volume of spent acid is withdrawn at a quiet zone at the bottom of the circulating path. Fresh hydrocarbon feed is added at a zone of turbulent downflow of cool acid. Product nitrobenzene can also be withdrawn continuously, either with the spent acid or from a separate settling zone in the organic phase. The nitrating (fortifying) acid for nitrobenzene is about 63% sulfuric acid (anhydrous), 36% nitric acid (as 100%) and 1% water. The low water content may be achieved with an easier-to-obtain 85% nitric acid by using sulfuric acid with a negative water content—that is, an oleum which contains free SO_3 dissolved in 100% acid, for example, 60% oleum containing 60% free SO_3 .

Under these conditions the spent acid will have very little nitric acid and will contain about 15% water. It can be denitrated by blowing with steam or air and then reconcentrated.

Reaction times may be of the order of 3 h for a batch nitration, including 1.5 to 2 h of "cooking" at up to 90°C after all reactants have been added, and of the order of 4 h for continuous nitration, where there is slightly more unreacted material (benzene) available for recycle. The batch reaction yield may be as high as 98%.

After reaction, the raw product is washed with water, then neutralized with a sodium carbonate solution, rinsed again with water, and dried by blowing with air or distilled to produce pure dry product. Any dinitrobenzene remaining in the bottoms should be treated with caution, as it is a sensitive, explodable material (wash out chemically or distill under vacuum).

Nitration of Toluene

While benzene is mostly nitrated only to the first stage, mononitrobenzene, toluene is nitrated beyond the first stage to a large extent. This is true not only in wartime when large amounts of trinitrotoluene (TNT) are required, but also in peacetime when 2,4-dinitrotoluene is desired in ever-increasing quantities for making polyurethane (polyisocyanate) rubberlike materials. The

dinitrotoluene is reduced to tolylene diamine and then reacted with COCl_2 to make the diisocyanate, which is reacted with polyols to make the desired products.

Toluene, having an ortho-para directing group on the ring, is more reactive than benzene. Under the same nitrating conditions, toluene will react about 11 times as fast as benzene to give mononitrotoluene. The second nitro group goes in less readily than the first, so nitrating conditions for dinitro product must be made more stringent than for the first group. Rather than raising temperature to cause the second nitro group to enter, the mononitro product is isolated and a fresh mixed acid is provided for the second stage, since the spent acid from the first stage will have been diluted by the water from the initial reaction. The presence of the methyl group, which can be oxidized by nitric acid or oxides of nitrogen at higher temperatures, makes it undesirable to use temperature as the sole means of increasing nitration potential.

The nitrating acid for toluene can be less concentrated than for benzene, e.g., about 58% H_2SO_4 , 30% HNO_3 , and 12% H_2O . For a batch reactor, the reaction may be started at 30°C with a heel of spent acid, then brought to 50°C as fresh mixed acid is added. The reactor would then be held at 50°C for about 2 h, making the total time about 3 h.

Here again, continuous nitration may be used under similar conditions. Efficient heat removal and agitation is of paramount importance. The heat of nitration for toluene is similar to that for benzene (about 27 kcal/g-mol).

The isomer distribution in the product will be about 62% ortho, 34% para, and 4% meta. These ratios are not particularly sensitive to acid composition or temperature. There is a slight tendency for the meta content to increase with temperature; this might possibly be ascribed to the oxidative side reaction, which may reach as much as 4% with mixed acids. The oxidation products would be generally meta-directing. The heats of reaction for the three isomers are slightly different, as shown in Table 2. It will be noted that the total heat of reaction to introduce two nitro groups is: 52.6 for m-dinitrobenzene, 53.5 for 2,4-dinitrotoluene via the ortho isomer first, and 55.0 for 2,4-dinitrotoluene via the para isomer first. The last two agree within the accuracy of the data, as they should.

TABLE 2	
Nitration Product	Heat of Nitration (kcal/mol)
Nitrobenzene	27.0
m-Dinitrobenzene	25.6
o-Nitrotoluene	25.3
m-Nitrotoluene	29.4
p-Nitrotoluene	33.7
2,4-Dinitrotoluene	<div> { 28.2 from <i>ortho</i> mononitrotoluene 21.3 from <i>para</i> mononitrotoluene </div>

In designing the heat transfer surface for a reactor, the heat of dilution of the nitrating acid should be taken into account. This can amount to 10 to 20% more heat to be removed.

For most commercial purposes the mononitrotoluenes are not separated, but washed as in the case of nitrobenzene and then nitrated further in a reactor with a separate range of acid concentrations and at a higher temperature, 70°C or above. The dinitro product, after washing and purification, is a mixture of about 72% 2,4-isomer and the rest, mostly 2,6-isomer (small amounts of 3,5 may also be present). This product is used directly for isocyanate manufacture.

For TNT manufacture, still higher strengths and temperatures are used for the third nitro group, often conducted in the same reactor as the dinitration. The final temperature may be of the order of 100°C. For high production rates during wartime, very short batch reaction times (e.g., 40 min total) at somewhat higher temperatures have been used, at some sacrifice in yields to oxidation products.

Nitroglycerine Manufacture

Nitroglycerine, or glyceryl trinitrate, a pale, oily liquid, is very sensitive to shock. The traditional method of manufacture used a moderate-sized batch reactor charged with about 6800 lb mixed acid (50% of nitric acid and an oleum equivalent to 52% of sulfuric acid). Cooling coils in the well-agitated reactor keep the temperature below 25°C as about 1300 lb glycerine are added in a slow steady stream (over a period of an hour). As the reaction approaches completion, the temperature is lowered to about 15°C. If the temperature rises above prescribed limits, the whole nitrator batch is dumped into cold water in a drowning tank on the floor below the nitrator. At the end of glycerine addition, the batch is allowed to settle for a few minutes, then the acid layer is decanted into another tank where it is allowed to settle further to recover more product. Meanwhile the nitroglycerine (about 3000 lb) is washed with warm water, then with weak (23%) sodium carbonate solution, then with a strong salt (NaCl) solution to break any emulsion and dehydrate the product. The finished nitroglycerine will still contain some 0.5% water. It is stored in small, lead-lined, rubber-covered tanks kept well apart. The spent acid, containing about 75% sulfuric acid and 10% nitric acid, is denitrated and then reconcentrated.

More recently several continuous nitroglycerine processes have been developed (Schmid-Meissner, Biazzi, Gyttop, Hercules) in which the nitration is carried out at much higher temperatures but at very short residence times. The reactor inventory can be very small and the hazardous equipment fully automated behind reinforced concrete walls. Typical of these is the Swedish Gyttop process.

The glycerine (or a mixture of glycerine and ethylene glycol, if so desired) is preheated to 50°C and the mixed acid is precooled to 05°C. The two continuous streams meet in an injector nozzle which forms an emulsion of the two, which then moves through a short length of pipe providing about 0.5 s residence time for a unit making 2000 lb/h nitroglycerine. The temperature rises to about 46°C; the emulsion is immediately cooled in an efficient heat exchanger to 15°C and then sent to a continuous centrifuge which separates the acid layer from the organic layer. The organic layer is reemulsified with water, separated in a hydroclone, then washed with sodium carbonate solution and finished in the usual fashion. The acid is further settled, then denitrated and reconcentrated. The critical parts of the system (injector, cooler, and separator) contain only about 30 lb nitroglycerine and are behind 1-ft thick reinforced concrete walls on three sides. The fourth side is open to an uninhabited restricted access area. The whole operation is automated. The product is removed from the process side through the wall into smaller, rubber-covered tanks holding about 15 gal, moved on rubber-tired dollies sometimes called "angel buggies."

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Olefin Processes

Yee Chien Hu

Part A

Crude/Residual Oil Cracking

Introduction

Ethylene and co-products are produced from steam cracking of hydrocarbons such as ethane, propane, butane, naphtha, and gas oil in tubular reactor coils installed in externally fired heaters (Fig. 1). Due to uncertainty of oil prices, depression of product prices, overcapacity of olefins facilities, and oversea competition, the olefins industry has struggled to maintain minimum cost and process flexibility. During the past decades, various research and developmental work were pursued to find processes using alternative feedstocks and providing cost advantages.

Alternative processes included heavy oil cracking processes, ethanol dehydrogenation, syngas-based processes, dehydrogenation of paraffins, oxidative coupling of methane, olefins disproportionation, and catalytic pyrolysis. In this article, the state-of-the-art of these processes is reviewed.

Heavy Oil Cracking Processes

To avoid dependence on oil refineries or gas processors to supply feedstocks, processes for the cracking of crude oil directly were developed by various companies [1]. Also, because of the tendency of converting industrial oil fired equipment to coal burning equipment, considerable quantities of residual oil will be released. A technology for cracking residual oil similar to the crude oil cracking process was also developed.

Since tubular-furnaces are inadequate to deal with the high severity and coking tendencies of heavy feedstocks, most processes developed for crude oil cracking are based on nontubular reactor principles (Fig. 2). These include Lurgi sand cracker, BASF fluidized coke process, BASF fluidized flow process, UBE process, coke heat-carrier process (KK process), ACR process, PCC process, and TRC process. The COSMOS process utilizes a tubular reactor with molten salt. The concepts and statuses for these processes are summarized in Table 1.

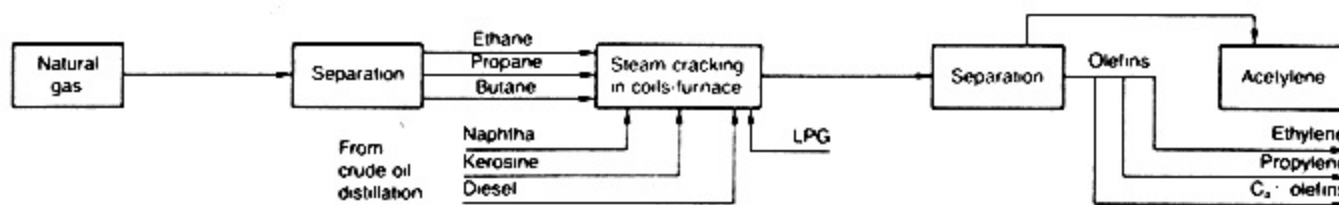


Fig. 1.
Conventional olefin process technology

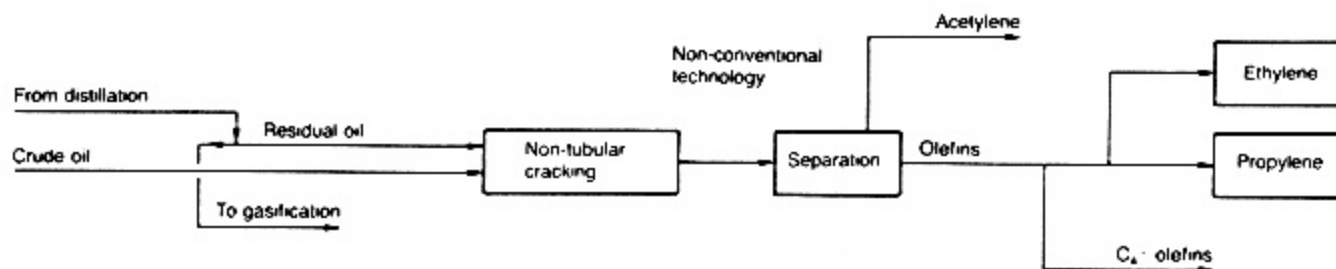


Fig. 2.
Crude/residual oil cracking for olefins.

TABLE 1 Crude or Residual Oil Cracking ProcessesConcept and Status			
Process	Developers	Process Concept	History and Statu
Sand Cracker	Lurgi Co., Germany	Heat carrier consists of fine grained sand that has been heated in a conveyor tube by a fuel oil flame. The sand is recycled and the oil is cracked in a fluidized bed reactor.	A 3040 MMlb/yr ethylene commercial operation at Dormagen, Germany, si was run in the pilot plant; naphtha wa commercial scale.
Fluidized Coke Cracking	BASF, Germany	Partial combustion in reactor to provide heat. Use a fluidized bed with coke particles. Coke is withdrawn as product.	Small scale 3060 kg/h feedstock and ton/h were tested in late 1950. A cor 80 MMlb/yr ethylene was operated at Germany, in early 1960.
Fluidized Flow Cracking	BASF, Germany	Similar to fluidized coke cracking process, except a regenerator is used to burn excess coke.	A fluidized flow process pilot plant with operated in early 1965. A 100 MMlb/yr flow was started up in 1970 at BASF's and was reported to have closed dov
UBE Process	UBE Ind., Japan	Partial combustion with oxygen in a fluidized bed using inorganic oxide particles as heat carrier.	A 5 ton/d crude oil pilot plant built in 1 more than 5 years. A 250 ton feedst plant was reported in 1979.
Coke Heat-Carrier Process (KK process)	Original developed by Kunugi & Kunii, then improved by Japanese Agency of Industrial Science & Technology (AIST) with five Japanese companies (Chiyoda, Toyo Soda, Maruzen, Mitsui, Mitsubishi).	Fluidized bed reactor using coke as heat carrier. Excessive coke is regenerated. Residue oil is used to generate low-calorie gas.	Extensive lab development complete crude oil pilot plant was started in Oct different runs (400 h) were conducte Mitsubishi and Chiyoda improved the h) at the end of 1973. A pilot plant w vacuum

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Process	Developers	Process Concept	History and Status
			residue was completed at the end of 1979. Test operation was completed in 1980.
ACR Process (Advanced Cracking Reactor)	Union Carbide, Kureha & Chiyoda (Japan)	Superheated steam produced by partial combustion was used as the heat carrier. Reactor designed to achieve low residence time. Uses steam as the heat carrier. Steam is heated by partial combustion.	Since 1970, a semicommercial plant has operated at Nakoso, Japan, by Kureha. T 2000 b/d of various crudes. In 1973, Kureha commenced codevelopment with Un Chiyoda. A pilot-size reactor was operated in Carbide's South Charleston Technical yield pattern. A rocket stand reactor test was conducted in 19761977 in California. demonstration unit with 5 MMlb/yr ethylene was completed at Union Carbide's Sea 1979. Debugging was completed in June 1980. The demonstration unit was operat half on a wide range of liquid feedstocks. The experimental program was complete
PCC Process	Dow		A 1 ton/d olefins pilot plant was operated for 200 d in 1979 with various feedstock. prototype facility, including the reactor, quench, acid gas cleaning and purification, ethylene, was completed in Freeport, Texas, in 1984.

(continued)

TABLE 1 (continued)

Process	Developers	Process Concept	History and Status
TRC Process (Thermal Regenerative Cracking)	Gulf Chemical, Gulf Canada, Stone & Webster	Fluidized reactors, solid heat carrier with generator.	Bench-scale development work was completed Cedar Bayou, Texas, was started in September pilot plant was vacuum residue, and a 15-mon completed.
COSMOS Process (Cracking Oil by Steam and Molten Salts)	Mitsui, Japan	Uses molten salts as both the heat carrier and catalyst to prevent coke formation. Uses an external heated tubular furnace.	A 5 kg/h oil bench-scale reactor was operated

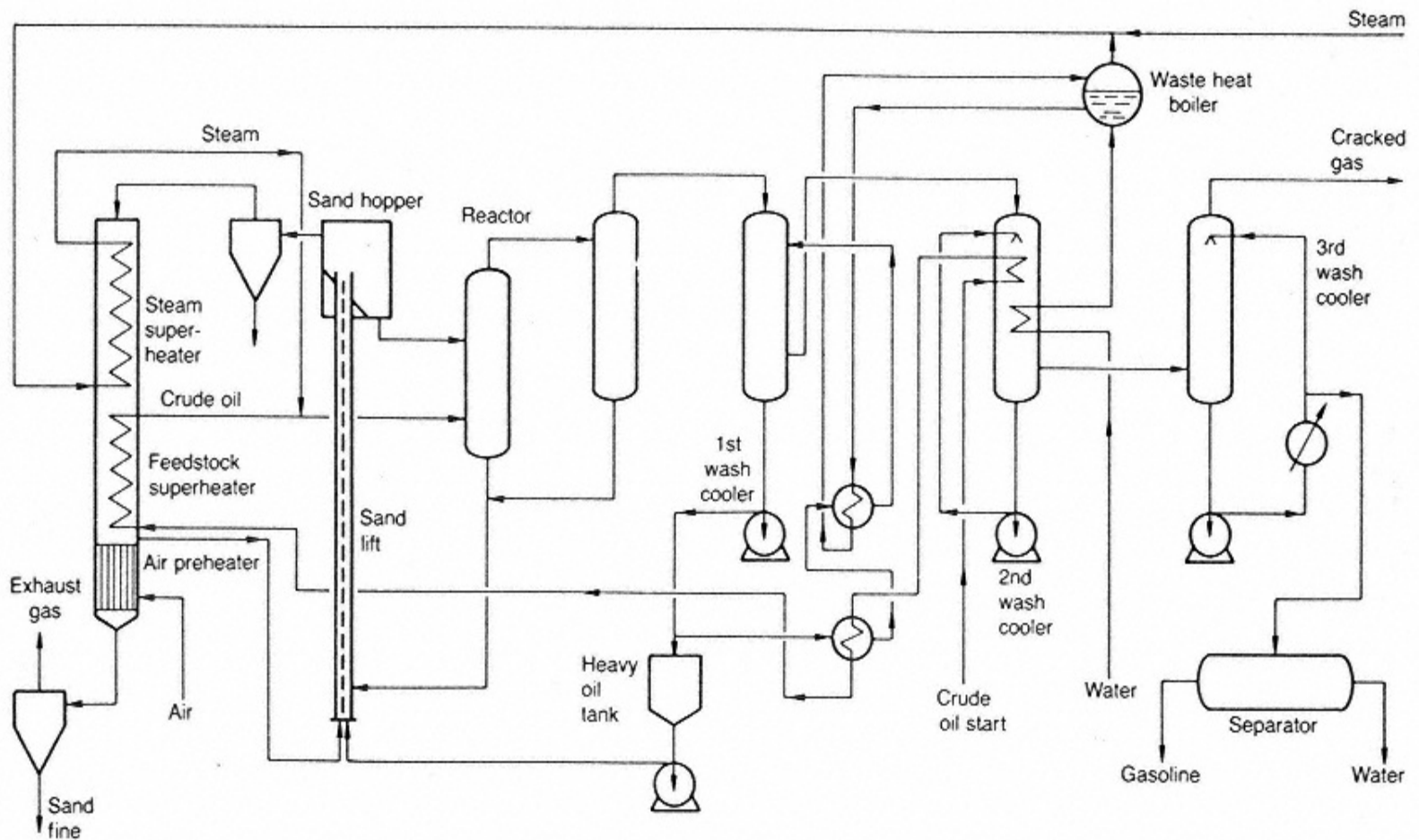


Fig. 3.
Lurgi sand cracker.

Lurgi Sand Cracker (Fig. 3)

Crude oil, after being heated to 655750°F in a superheater, is injected into the fluidized bed of hot sand in the reactor together with steam. The hot sand heats the hydrocarbons up to 13001550°F. The reaction time in the fluidized bed is between 0.3 and 0.5 s. Sand is continuously removed from the reactor to a sand lift regenerator where the coke is burned off and then the hot sand is returned to the reactor. This process can crack ethane through residue oil. The process is flexible; the propylene to ethylene ratio can vary between 0.3 to 0.9. However, mechanical attack from the circulating sand on the refractory lining was reported during early development of this process.

Typical cracking yields for Iraq Crude are shown in Table 2.

TABLE 2 Cracking Yields for Sand Cracking

Feed	Iraq crude	
	1350	1390
Cracking temperature, °F		
Yield, wt. %:		
Ethylene	19.6	23.1
Propylene	12.6	12.8
Butadiene	3.4	3.7
n- and i-Butylene	4.7	2.0
C1C4 paraffins	13.8	14.4
Gases	3.4	2.4

Gasoline up to 428°F	17.0	16.5
Oil above 428°F	20.5	22.1
Carbon on sand and losses	5.0	3.0

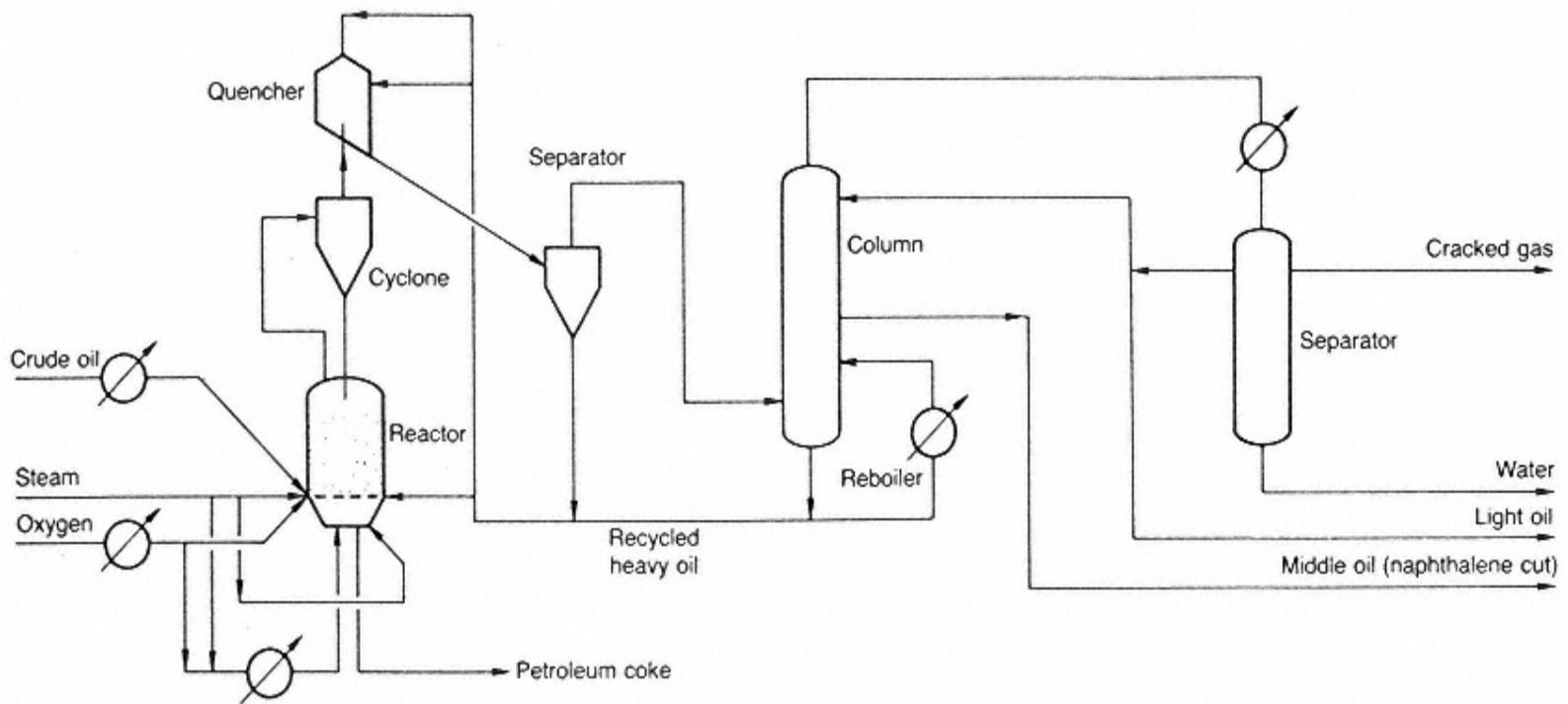


Fig. 4.
BASF fluidized coke cracking process.

BASF Fluidized Coke Cracking (Fig. 4)

A mixture of preheated steam and oxygen is blown in under the reactor grid. Coke is used as the heat carrier in the reactor. The preheated crude oil and the recycled heavy oil are introduced into the fluidized bed. The reactor is kept at 1290 to 1380°F. The steam-to-crude ratio is 1:1; the effective flow velocity is 0.7 m/s. Vapors from the cyclone are fed to the quencher where they are cooled to 570°F.

Typical cracking yields for Minas and Libyan Crude are shown in Table 3.

BASF Fluidized Flow Cracking (Fig. 5)

This process is similar to the BASF fluidized coke cracking process except that there is a regenerator which can burn the coke formed during cracking reactions. The reactor consumes the heat generated from combustion in the

TABLE 3 Cracking Yields for Fluidized Coke Crackers

	Feed	
	Minas Crude	Libyan Crude
Cracking temperature, °F	1340	1370
Steam/feed	1	1
Yield, wt. %:		
Ethylene	23.0	20.6
Propylene	12.5	11.6
Butylene + butadiene	6.0	4.5
Ethane	4.5	4.6
Pyrolysis light oil	14.0	16.6

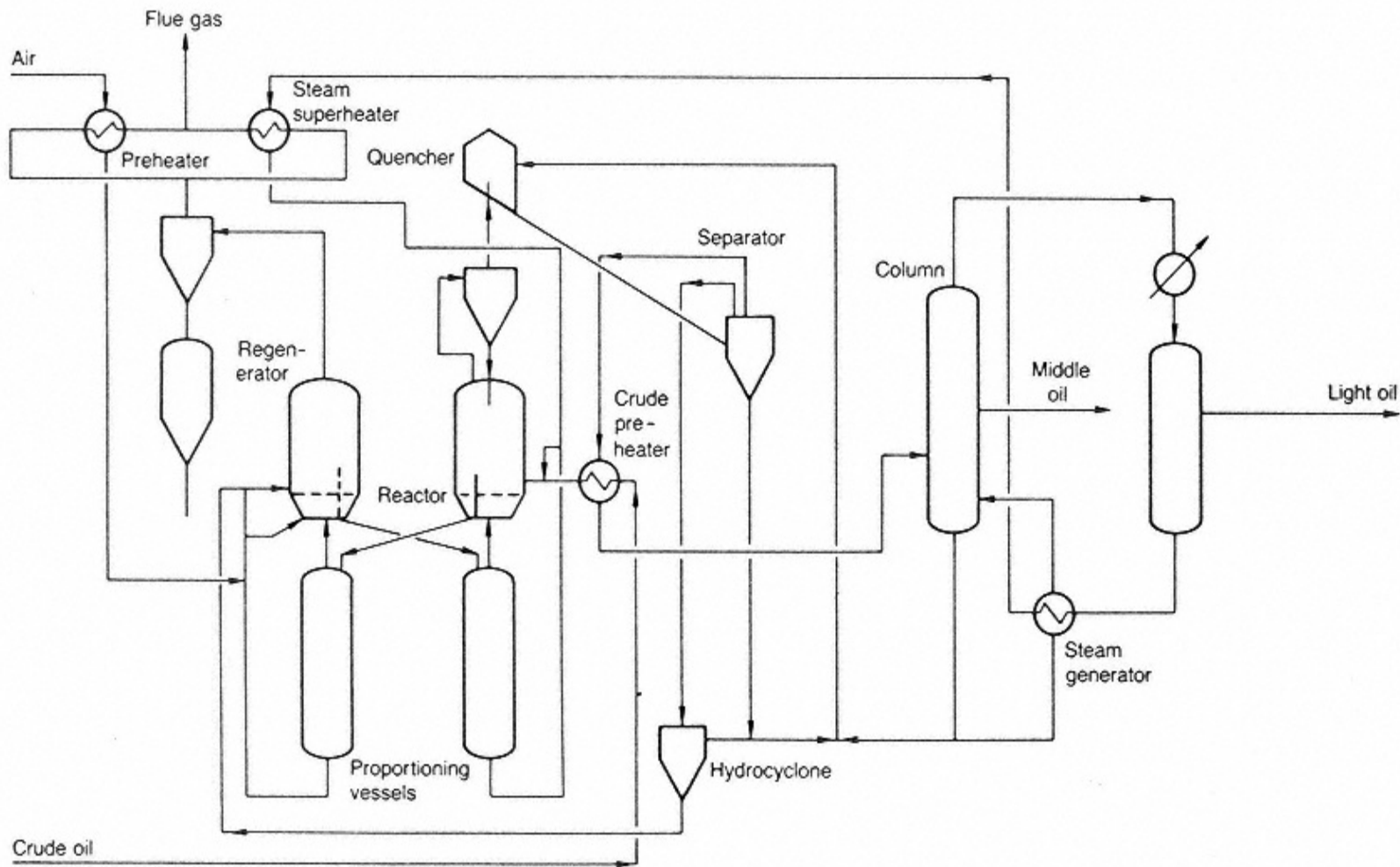


Fig. 5.
BASF fluidized flow cracking process.

regenerator. Air is needed for the fluidized flow process. The cracking temperature in the fluidized flow process is higher than that in the fluidized bed process, and the ethylene yield is higher. Cracking yields for a pilot-scale fluidized flow unit are shown in Table 4.

UBE Process (Fig. 6)

The fluidizing gas (steam) and oxygen are supplied to the bed through the gas distributor. A fluidized bed of inorganic oxide particles (mullite) serves as the heat carrier. Crude is heated to 750°F in a pipe still and blown into the bottom of the fluidized bed of mullite particles. Cracking is performed at the

TABLE 4 Cracking Yields for Fluidized Flow Process

	Feed	
	Minas Crude	Libyan Crude
Cracking temperature, °F	1400	1400
Yield, wt. %:		
Ethylene	25.0	22.0
Propylene	11.2	10.5
Butylene + butadiene	5.3	5.8
Ethane	4.3	3.7
Pyrolysis light fuel oil	17.5	22.5

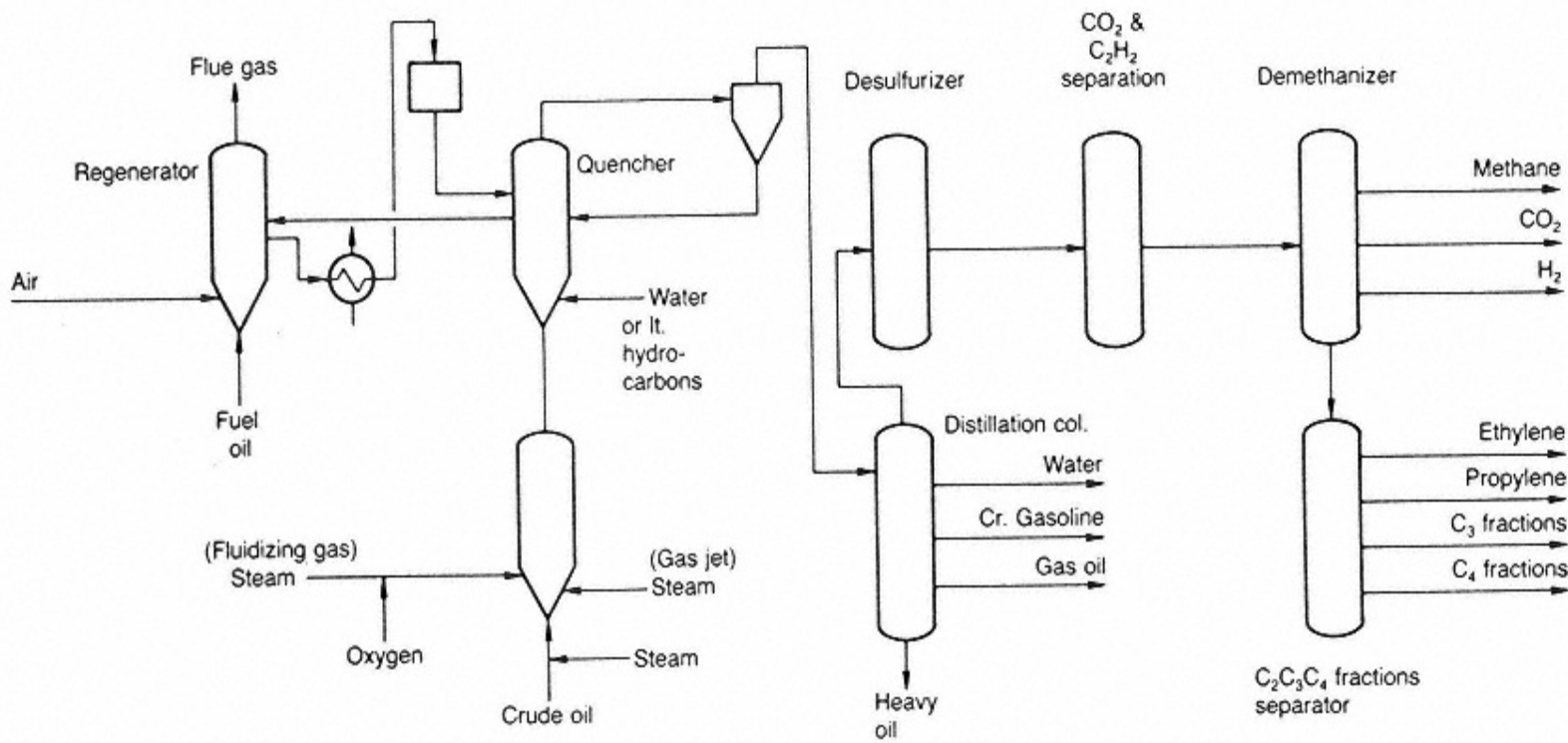


Fig. 6.
UBE process.

temperature attained by partial combustion. The cracking temperature can be held as high as 1530 to 1615°F. Residence time is around 0.2 to 0.3 s. Velocity of the gas jet stream is 25 to 35 m/s. The superficial gas velocity in the bed is maintained at 6 to 7 m/s. A continuous regeneration system removes coke from the particles. The cracking yields for a pilot plant are shown in Table 5.

Coke Heat-Carrier Process (KK Process) (Fig. 7) [2]

This process was originally developed for crude oil processing. During the pilot-plant study stage, the feedstock was shifted to vacuum and atmospheric residues.

Residue oil is heated to 750°F in the pipe still. The coke particles are heated to about 1830°F and introduced to a fluidized coke bed reactor, where cracking is done at 1380 to 1470°F to produce ethylene. Tar in the residue is deposited on coke particles and burned in a heater. The stability of this process is demonstrated by pilot runs at different stages. The latest patent

TABLE 5 Cracking yields for UBE Process

Feed	Crude oil
Cracking temperature, °F	1544
Residence time, s	0.20.3
Yield, wt. %:	
Ethylene	28.1
Propylene	11.3
C4 fraction	8.4
Cracked gasoline	12.2
Heavy oil	4.4

Other off-gas

66.6

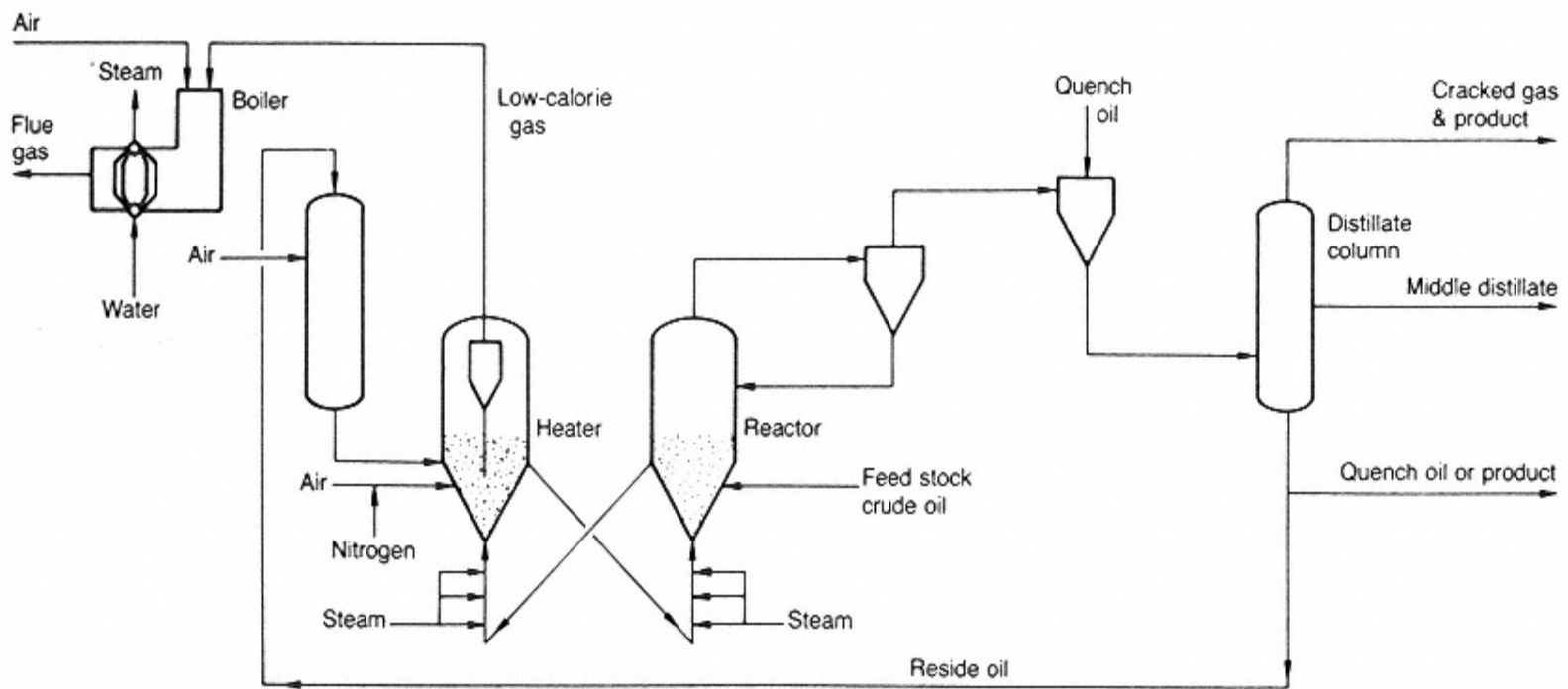


Fig. 7.
Coke heat-carrier process (KK process).

indicates that the residue oil produced is used to make low calorie gas for heat recovery. The cracking yields for the coke heat-carrier process are shown in Table 6.

TABLE 6 Product Distribution Data for Coke Heat-Carrier Process

	Feed Oil		
	Paraffins Atmospheric Residue	Atmospheric Residue	Vacuum Residue
Cracking temperature, °F	1382	1384	1384
Weight ratio of steam to oil (wt./wt.)	1.0	0.99	0.97
Residence time, s	3.24	3.61	3.87
Product wt. %:			
Gaseous			
H ₂	0.6	0.6	0.6
H ₂ S	0.1	0.6	1.5
CH ₄	13.7	12.6	11.0
C ₂ H ₂	0.1	0.1	0.1
C ₂ H ₄	23.8	16.8	12.4
C ₂ H ₆	4.0	4.1	3.6
C ₃ H ₄	0.2	0.2	0.1
C ₃ H ₆	10.1	8.6	6.7
C ₃ H ₈	0.4	0.4	0.3
C ₄ +	3.9	3.4	2.6
Total	56.9	47.4	38.4
Liquid			
C ₅ -390°F	18.0	16.0	11.1
390°F+	23.0	32.8	36.1
Total	41.0	48.8	47.2
Coke	2.1	3.8	13.9

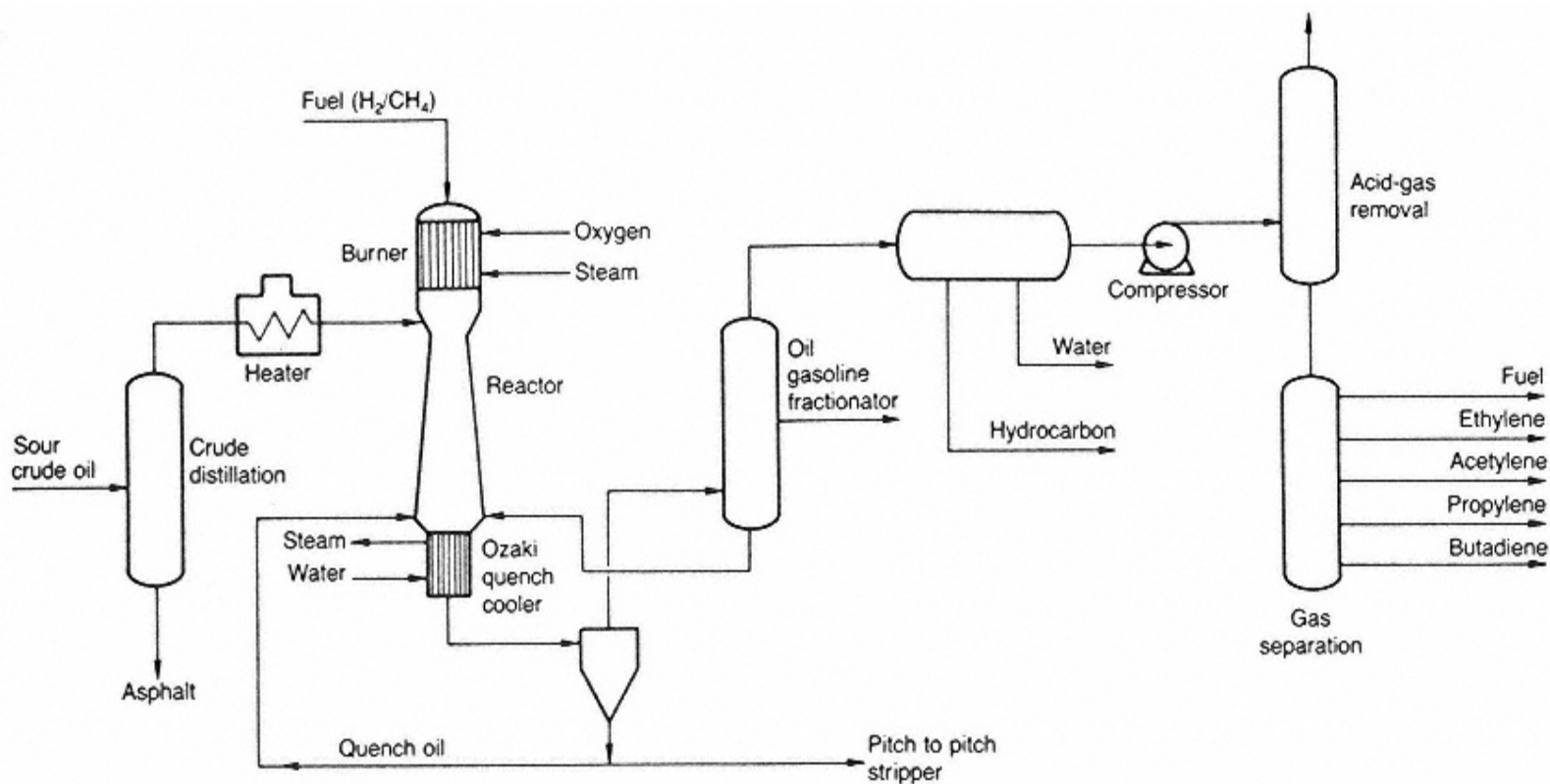


Fig. 8.
ACR (advanced cracking reactor) process.

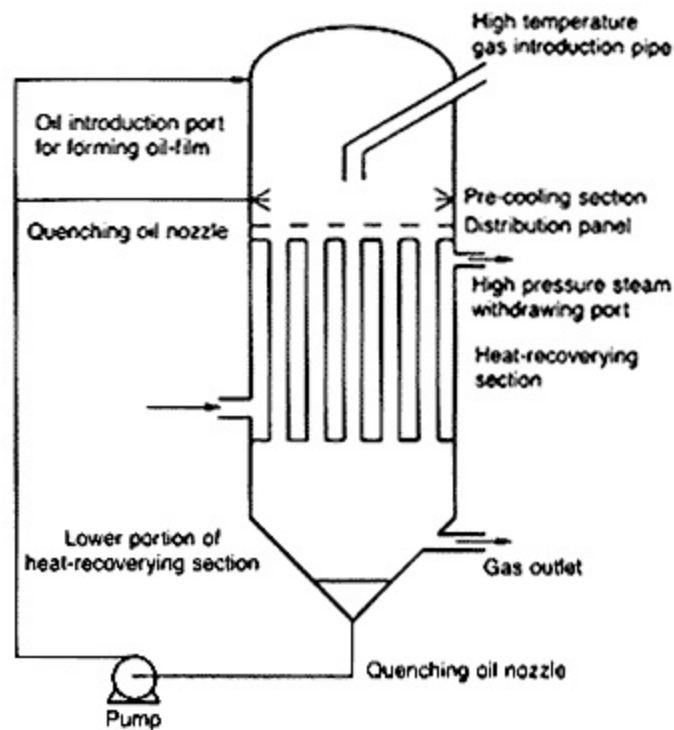


Fig. 9.
Ozaki quench cooler.

ACR (Advanced Cracking Reactor) Process (Fig. 8) [3]

The ACR process was developed jointly by Union Carbide, Kureha Chemical Industry Co., and Chiyoda Chemical/Construction Co. This process was developed to use crude oil and residue cracking. During the development stage, the high Conradson carbon of residue fractions with low ethylene yield were found not to be economically attractive. Light fractions were tested.

The keys of this process are high temperature, short residence time, and low hydrocarbon partial pressure. Superheated steam is used to provide heat for the cracking reaction. The burner, fired by fuel and oxygen, creates the 3600°F heat carrier. The cracking reaction is carried out at 1690-1760°F with a 0.01-0.02-s residence time. The key to the performance of the reactor is to get efficient mixing of the feed oil and superheated steam. The reactor following the burner is the most critical element of the process. Extensive work has been done to insure that the fluid dynamics of the reactor are adequate. The Ozaki quench cooler (Fig. 9), which cools down the reactor effluent, is specially designed to avoid fouling problems. Quench oil recycle conditions control the quality of pitch.

Operating conditions of the ACR process are flexible enough to give a propylene: ethylene ratio of 0.17 to 0.63 and an acetylene: ethylene ratio, which can be adjusted, from 0.04 to 0.13. Typical cracking yields are shown in Tables 7 and 8.

ACR olefin yields are compared with conventional olefin yields for naphtha and atmospheric gas oil feedstocks in Table 8.

TABLE 7 ACR Process (feedstock flexibility: lb/100 lb feed)

	Feed			
	Naphtha	Atmospheric Gas-Oil	Vacuum Gas-Oil	Whole Distillate
Ethylene	37.5	30.9	26.4	31.7
Propylene	15.8	10.7	10.5	11.6
Butadiene	10.2	8.1	7.4	7.8
H ₂ and fuel gas	13.9	11.7	11.6	11.5
Pyrolysis gasoline	16.8	20.2	11.4	19.5
Pyrolysis fuel oil	5.8	18.4	32.7	17.9
	Source of Feed			
	Arabian Light	Libyan	Arabian Heavy	Arabian Light
API gravity	66.4	41.0	21.8	39.4
Boiling range, °F	C5-300	300-650	650-1050	C5-1050

TABLE 8 Comparison of Olefin Production (lb/100 lb feed)

	C5-400°F Naphtha		400-650°F Atmospheric Gas-Oil	
	ACR	Conventional	ACR	Conventional
Ethylene	30.0	23.4	30.5	22.5
Propylene	14.1	17.2	11.5	15.4
Butadiene	10.6	11.8	8.8	11.4
Pyrolysis gas	29.9	29.5	20.0	18.4
Light fuel oil	2.1	2.5	6.0	14.6
Heavy fuel oil	3.6	2.4	12.1	7.5
Fuel gas	12.0	13.1	11.1	10.1

PCC Process (Fig. 10) [4]

The PCC (partial combustion cracking) process was developed by Dow Company. It is a direct cracking process in which the heat of the reaction is supplied by combustion of a portion of the feedstock. This process can convert whole crude, fuel oil, and other heavy petroleum fractions to olefins and aromatics with a minimum production of fuel oil or residue.

The basic reactions in the Dow PCC process are oxidation, shift, and cracking. These steps are performed in specially designed reactors at 565 lb/in.² gauge, 2900-3600°F for the steam shift reaction, and 1290-1830°F for cracking. The ability to vary the composition of the combustion mixture by carrying out the shift reaction is critical to successful operation with a wide range of feedstocks. The integration drawing for the PCC process is shown in Fig. 11.

Table 9 shows a comparison of the yields between PCC and conventional technology. Table 10 shows the cracking yields for various feedstocks.

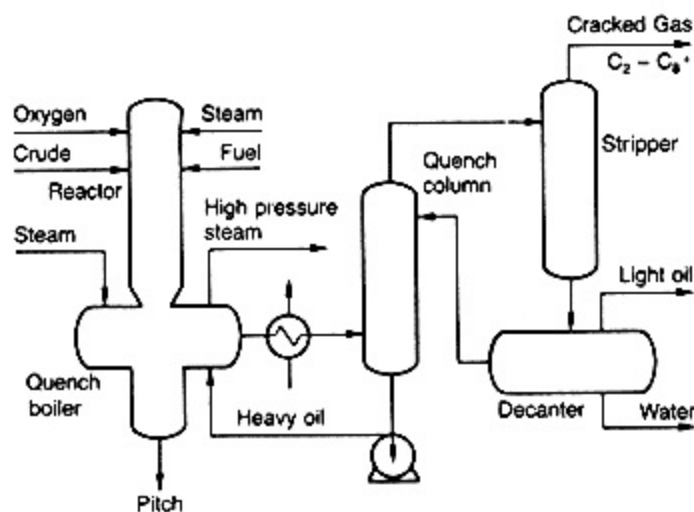


Fig. 10.
PCC (partial combustion cracking) process.

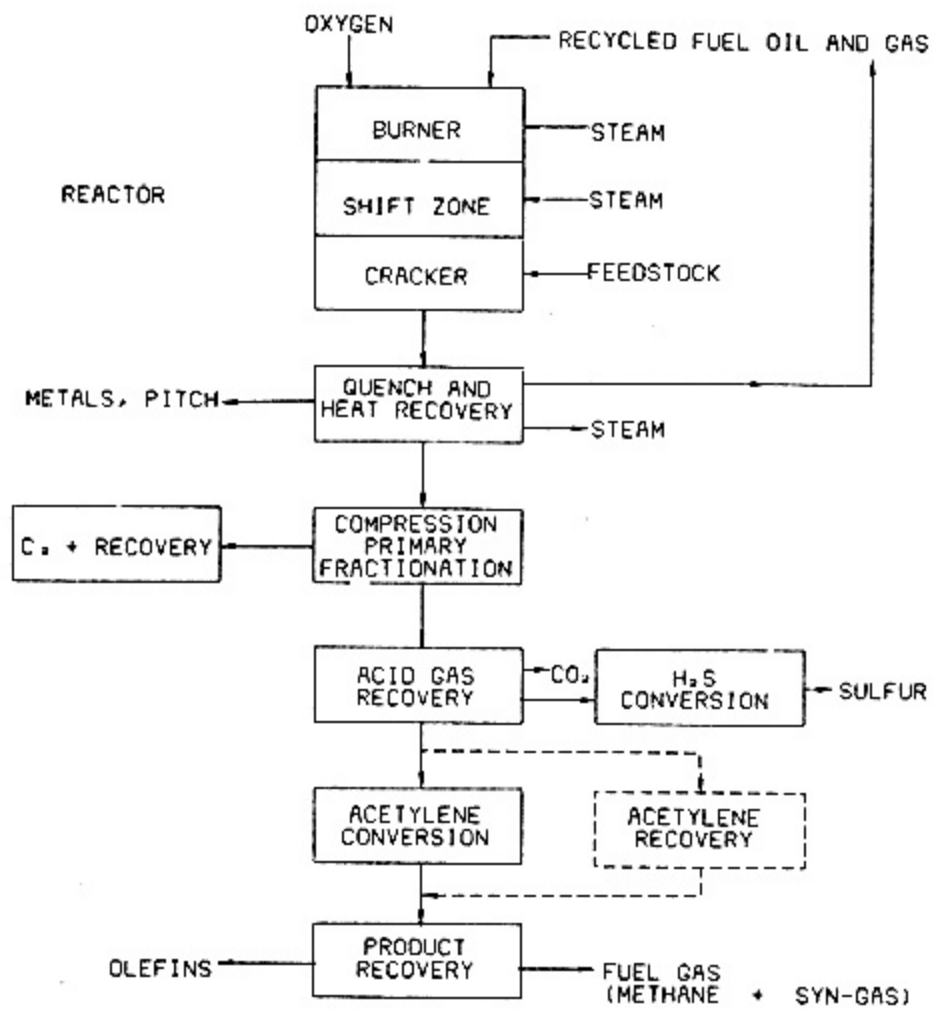


Fig. 11.
Integration drawing of the PCC process.

TABLE 9 Average Ethylene Yields (%)

Feedstock	PCC	Conventional
IBP-350°F naphtha	35	28
350-650°F gas-oil	32	23
30API crude oil	27	
Residual oil	25	

TABLE 10 Cracking Yields for PCC Process

	Feed	
	Crude Oil	650°F Residue Oil
Cracking temperature, °F	750°F higher than conventional	furnace limit
Residence time, s	0.1	0.1
Yield, wt. %:		
Methane	14.0	12.4
Acetylene	2.3	2.5
Ethylene	25.2	24.4
Ethane	1.9	1.6
Propylene	8.3	6.9
C4's	6.6	5.1
C5's	3.0	1.6
C6C7	20.2	14.3
C8 + fuel oil	15.7	28.5
Others	Balance	Balance

TRC (Thermal Regeneration Cracking) Process (Fig. 12) [5, 6]

This process was developed to use vacuum tar as the feedstock rather than crude oil, although crude oil can be handled. Heat needed for feedstock cracking is transferred directly from hot micron-size solid particles heated to 16001800°F in a moving stream. The reactor outlet temperature is approximately 1800°F. TRC residence times are compatible with coil cracking furnaces, and the steam-to-hydrocarbon ratio is 0.20.4. Coke forms on hot moving solids which can be regenerated. The solids loop is analogous to a raiser FCC loop consisting of a solids heater, multiple reactors, and the accessory transfer lines. For a range of cracking conditions, 2060 lb solid/lb hydrocarbons are required. The reaction occurs in a dense-phase fluidized

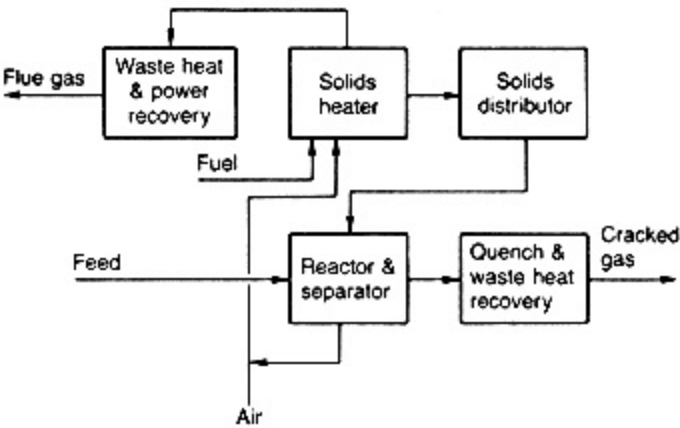


Fig. 12.
TRC (thermal regenerative cracking) process.

TABLE 11 Comparison of TRC with Conventional Process (lb/100 lb feed)

	Conventional	TRC
Gas	5.2	9.9
Olefins	48.8	46.1
Gasoline	18.5	20.7
Light pyrolysis oil	1.8	7.5
Heavy pyrolysis oil	10.1	0

bed. Severity, variety of feedstocks, and by-product recycle for this process have no limit.

A semicommercial field test unit has operated for 15 months at Gulf's Cedar Bayou Plant. This unit is a joint project between Stone-Webster and Gulf. Various operational aspects have been demonstrated, such as yields, solid-gas separation, stability and control, nonfouling system, and mechanical integrity. Stone-Webster is working on the integrated heavy oil pyrolysis (IHOPP) utilities novel processing steps in combination with proven coil technology to process heavy feedstocks. IHOPP technology will be incorporated into the TRC system.

Table 11 shows the net material balancing by comparing a conventional unit on atmospheric gas-oil and TRC processing with a paraffinic atmospheric residue.

COSMOS Process (Cracking Oil by Steam and Molten Salts) (Fig. 13)

This process cracks crude oil or heavy oil by using molten salts (Li_2CO_3 , Na_2CO_3 , and K_2CO_3 mixture system) which act as the catalyst for water gas reactions with coke. Conventional tubular reactor coils are used. A wet wall with molten salts on the internal surface of the reactor tube prevents plugging of the reactor tube at higher temperatures.

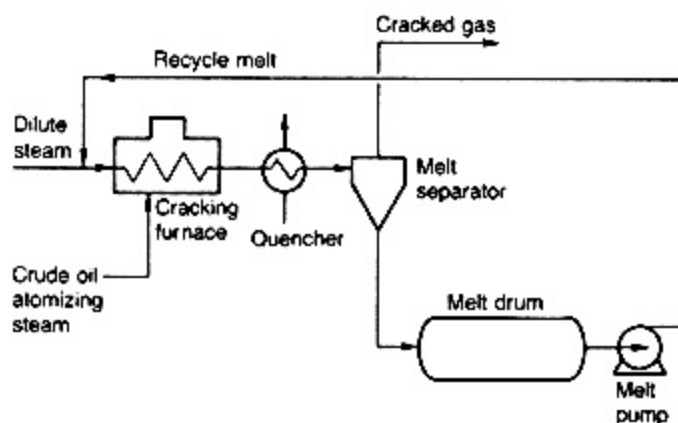


Fig. 13.
COSMOS (cracking oil by steam and molten salts) process.

Melt is sheared and atomized by a high velocity steam heated to 1380°F and fed into the cracking furnace. The mixture of preheated feedstock oil and atomized steam is injected into this furnace to undergo thermal cracking. Carbon pitch produced via thermal cracking does not adhere to the internal wall of the furnace tube due to the wet wall effect. The carbon and pitch are gasified by the water gas reaction through catalysis of the melt. The stream from the furnace, consisting of the cracked gas, steam, and metal, goes through a quencher and a cyclone and is separated into gas and liquid phases. The separated liquid-phase melt is recycled to the cracking furnace. The cracking yields from COSMOS pilot-plant data are shown in Table 12.

A comparison of various cracking processes is shown in Table 13. Lurgi's sand cracker and BASF's fluidized coke process and fluidized flow process pioneered moving bed reactor technology. Several commercial plants were reported in the early 1960s, yet no further commercial plants were built. Newer versions of the fluidized bed reactor process, like the UBE process, have higher ethylene yield, but with a large quantity of off-gas. The COSMOS process overcomes the coking problem of tubular furnaces, but severity and residence time seems not as good as for nontubular reactors. The operability of the coke heat-carrier process has been successfully demonstrated and its energy is very well balanced, yet the reactor residence time is high. The ACR process seems to have the highest severity, lowest residence, and highest ethylene yield among the processes reported. Detailed reactor information for the PCC process is not available; it is assumed to be similar to that of the ACR process. The TRC process has a residence time similar to conventional processes while avoiding coking problems.

All the above process development programs are inactive except for the TRC process. The TRC process has been fully demonstrated in a semicom-

TABLE 12 Cracking Yields for COSMOS Process

	Feed	
	Minas Crude 1470	Taching Crude 1470
Cracking temperature, °F		
Steam/oil, wt./wt.	1.33	1.33
Residence time, s	0.55	0.55
Melt/oil, wt./wt.	2.0	2.0
Yield, wt. %:		
H ₂ + CH ₄	15.71	14.56
Acetylene	0.31	0.30
Ethylene	25.74	25.19
Ethane	2.23	2.21
Propylene	11.71	11.19
C ₄ 's	6.11	6.65
C ₅ +	9.31	8.09
CO ₂	11.75	15.30
Fuel oil	25.06	28.39
Others	Balance	Balance

TABLE 13 Comparison of Crude or Residual Oil Cracking Processes

	Sand Cracker	Fluidized Coke Process	Fluidized Flow Process	UBE Process	Coke Heat- Carrier Process	ACR Process	PCC Process	TRC Process	
Feed	Crude oil	Crude oil	Crude oil	Crude oil	Crude residue	Heavy gas	Crude oil	Crude residue	
Cracking temperature, °F	1390	1370	1400	1544	1380	1760	1830	1800	
Steam/feed		1.0			1.06				
Residence time, s	0.30.4			0.20.3	24	0.015	0.1	0.25	
Oxygen	No	Yes	No	Yes	No	Yes	No	No	
Reactor	Fluidized bed	Fluidized bed	Fluidized bed	Fluidized bed	Fluidized bed	Partial combustion, rocket type	Partial combustion, rocket type	Fluidized bed	T n
Separator					Disengaging	Gas separation in fraction	Gas separation in fraction	Proprietary separator	

mercial unit. The use of catalytic solids with a TRC reactor has also been pursued. Overall, unconventional cracking processes have the advantages of nontubular flexibility in feedstocks, product-range flexibility, and high severity and low residence time in reactors. This gives them the potential to replace tubular reactors for processing light feedstock or cheap heavy stock.

Because of uncertainty in oil prices, crude oil or residuum cracking processes are still not feasible. However, if oil and gas prices rise again, residuum cracking may become attractive in the late 1990s.

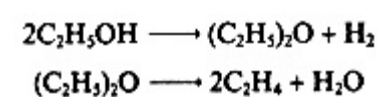
Part B

Ethanol Dehydration

A number of catalytic ethanol dehydration units were built in the 1950s and 1960s in Asia and South America. Some of them are still in operation, but others were shut down when new, large olefins plants based on steam cracking were brought on-stream [7].

Because of uncertainty in the availability of petroleum feedstock, a renewal of interest in ethanol dehydration exists. Ethanol can be produced either from biomass fermentation (Fig. 14) or by synthesis from syngas. Both ethanol manufacturing processes and syngas processes have been under rigorous development during the last decade.

Though the mechanism of ethanol dehydration has not been completely established, for practical purposes the following consecutive reaction sequence may be assumed:



These are endothermic reactions; temperature is the critical operating variable. In the industrial production of ethylene, yield is 94 to 99% of the theoretical value depending on the process scheme. Traces of aldehydes, acids, high hydrocarbons, and carbon dioxide, as well as water, have to be removed.

Industrial processes for ethanol dehydration are all based on the passage of ethanol vapor over solid catalysts at high temperatures. The preferred catalysts are activated alumina and phosphoric acid on a suitable support, or zinc oxide with alumina. Industrial reactors consist of fixed- and fluidized-bed processes. Fixed-bed processes can be operated either as isothermal or adiabatic. The reported processes include Lummus processes (fixed or fluidized process), Halcon/SD process, NIKKI process, and Petrobras process.

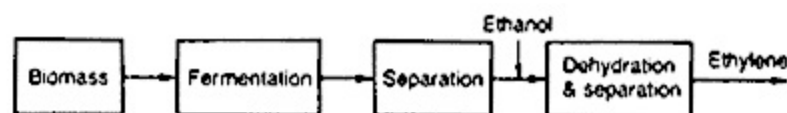


Fig. 14.
Ethylene from biomass through fermentation and ethanol dehydration.

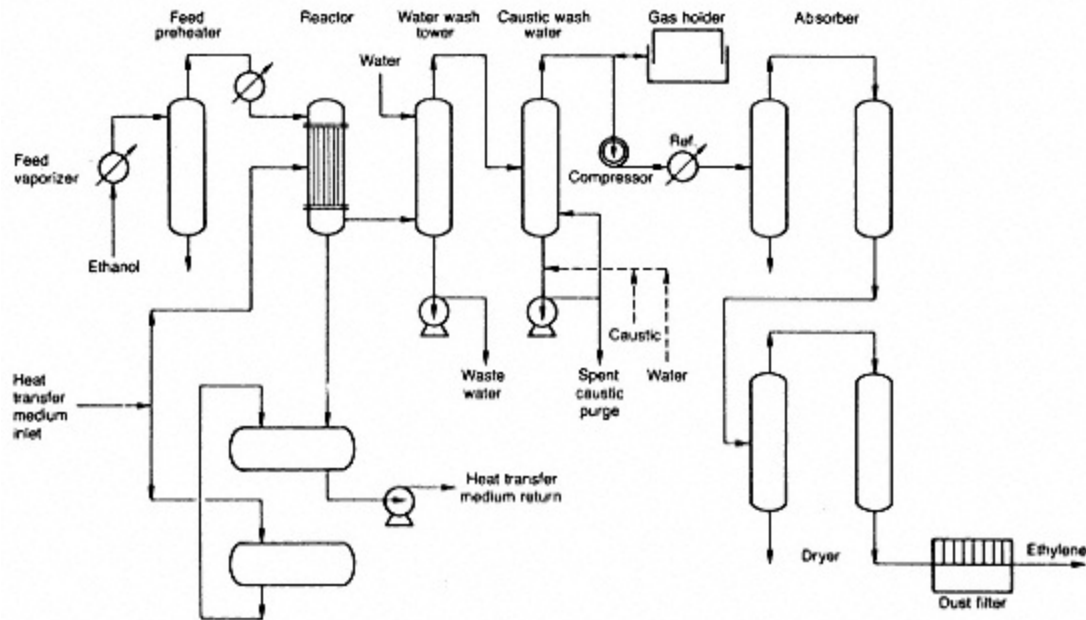


Fig. 15.

C-E Lummus fixed-bed process for ethanol dehydration.

Lummus Fixed-Bed Process (Fig. 15)

The ethanol feed is pumped into a vaporizer. The vapor is preheated with high pressure steam and passed over a catalyst of activated alumina for dehydration. Approximately 94% of the theoretical is dehydrated.

The required heat for the reaction is supplied by a consuming heat-medium in the reactor shell. The temperature, which is critical, is kept between 565 and 600°F. The catalyst is regenerated with air and steam every few weeks to remove any carbon deposits. The reaction effluent is scrubbed with caustic after a water quench and is then dried before feeding it to a purification system.

Lummus Fluidized-Bed Process (Fig. 16)

A fluidized-bed reactor can provide efficient heat and mass transfer. Efficient temperature control, which is desirable to optimize ethanol conversion and ethylene yield with minimum by-product formation, can be achieved. The required heat of reaction is supplied via circulation of a fluidized catalyst from the regenerator.

The Lummus pilot plant for fluidized bed ethanol dehydration indicates that an ethylene yield of 99% is obtainable compared to 94-96% yields with fixed-bed systems.

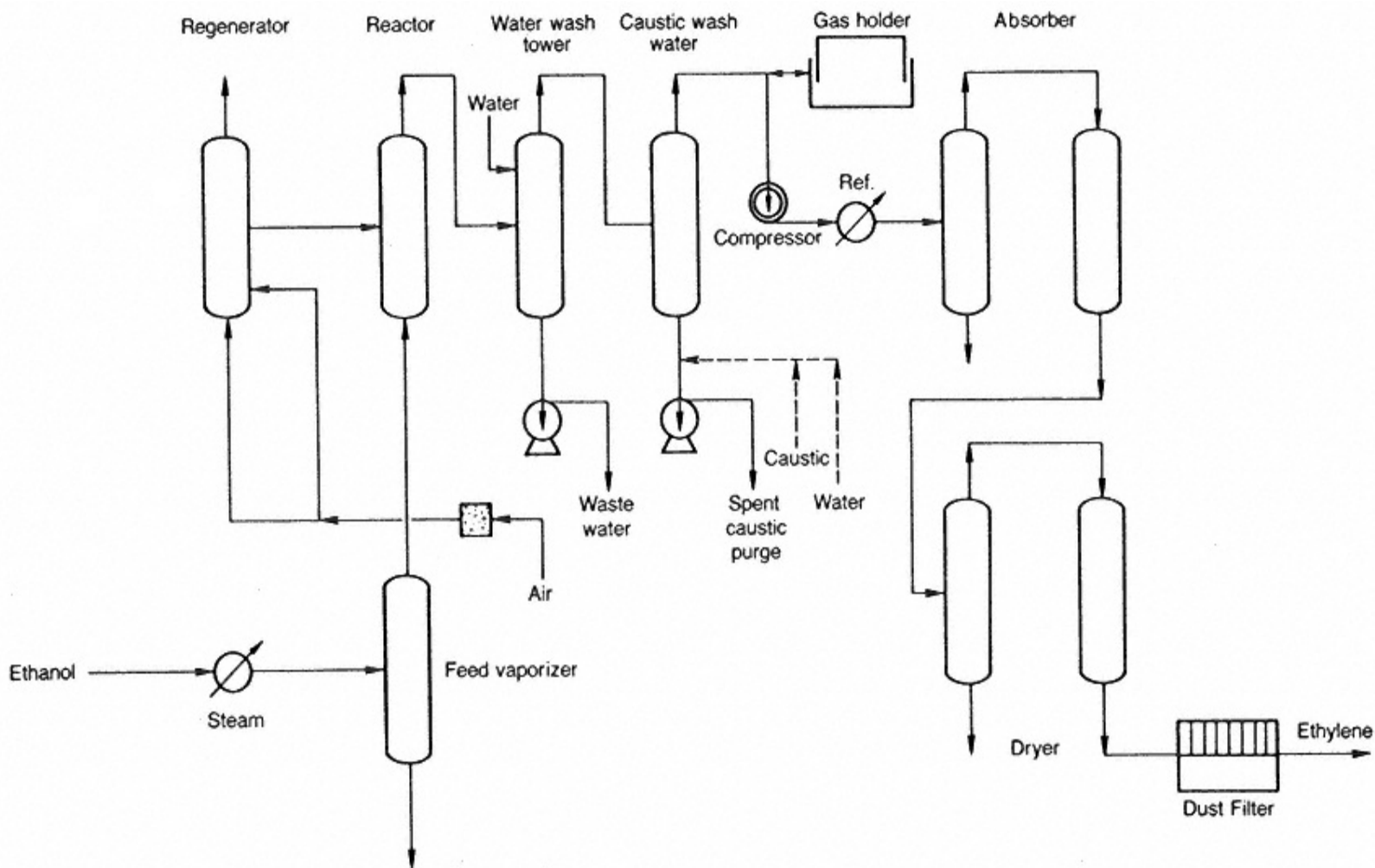


Fig. 16.
C-E Lummus fluidized-bed process for ethanol dehydration.

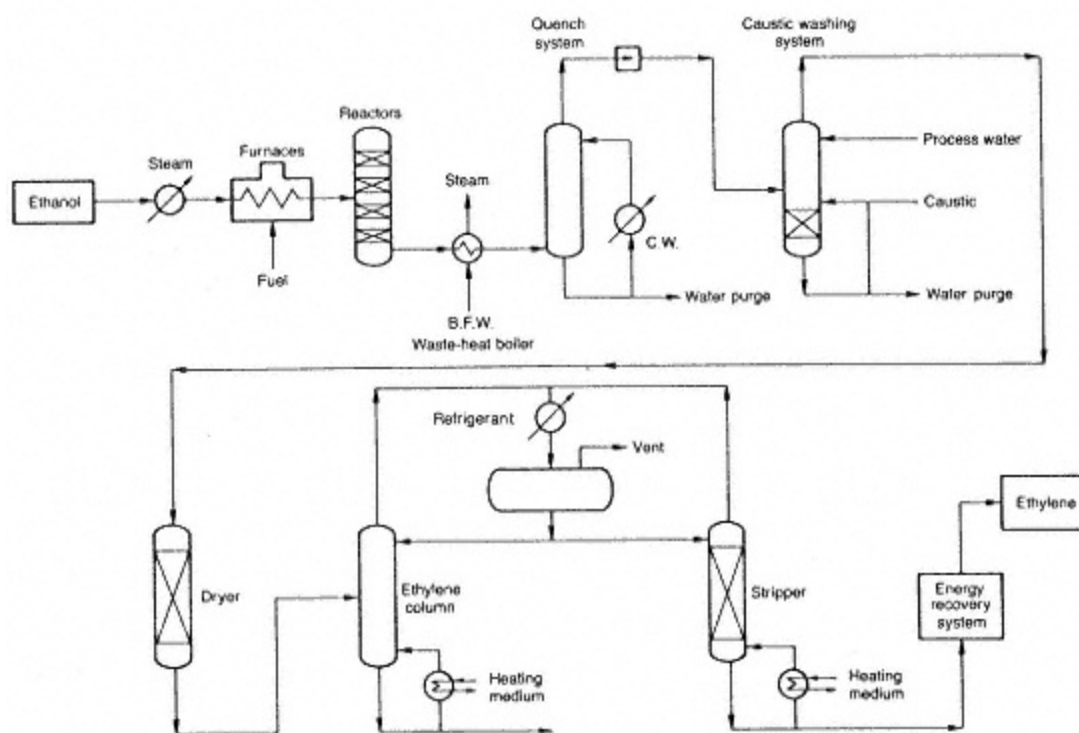


Fig. 17.
Hakon SD process for ethanol dehydration.

Halcon/SD Process (Fig. 17)

Halcon/SD has developed a new ethylene-from-ethanol catalyst name Syndol. The old catalyst has conversion of ethanol from 95 to 99.5%, but selectivity ranges from 80 to 96%. With the new catalyst, selectivity stays consistent for 8 months of operation without regeneration.

The Syndol catalyst has been claimed by SD to be rugged enough for use in an adiabatic reactor where the inlet temperature can be as high as 932°F. An adiabatic pilot plant with two reactors in series has been tested with Syndol catalyst. Selectivity above 99% was achieved (with conversion of 99.8%).

NIKKI/JGC Process

This process has been tested in a pilot plant in Brazil in cooperation with the Instituto Pesquisas Tecnologicas de Estado de São Paulo. The catalyst, developed by NIKKI (a JGC Subsidiary), maintained high activity over 3 months. A 97% yield was obtained, indicating that the catalyst could be used for around 1 year without regeneration in a commercial plant.

Petrobras Process

Petrobras has developed an adiabatic process in which ethanol and steam are fed into a series of fixed-bed reactors. This process results in lower by-product formation and increased catalyst life. A 60-ton/yr prototype plant was operated for more than a year in Brazil. A 60,000-ton/yr Petrobras adiabatic process was brought on-stream at Maceio, Brazil. In this process ethanol is preheated, vaporized, and mixed with steam, then passed at 842°F through a vertical tubeless reactor containing a catalyst. Conversion efficiency for this process is 98% versus 93% for isothermal. Economics of the adiabatic process come from savings in the cost of equipment and maintenance. Comparisons of ethanol dehydration processes are shown in Table 14.

In order to compete with conventional olefins processes, the ethanol dehydration process needs a cheap feedstock. With progress in biotechnology, cost reduction for biomass-based ethanol is possible. In addition, there is progress in syngas-based ethanol. This is discussed in the next section.

Overall, the advantages of biomass over fossil mass as the source of ethanol are renewable, flexible, and small-scale operation. However, cost is still a disadvantage.

TABLE 14 Comparison of Ethanol Dehydration Processes

Process	Concept	Yield (%)	Status
Lummus fixed-bed process	Fixed-bed isothermal reactor	94	A commercial plant was built in India
Lummus fluidized-bed process	Fluidized-bed isothermal reactor	99	Pilot plant
Hakon/SD process	Fixed-bed isothermal reactor. Can be operated at adiabatic mode. New active catalyst	96	Commercial plant for isothermal reactor, pilot plant for adiabatic reactor
NIKKI/JGC process	Fixed-bed isothermal reactor. New active catalyst	97	A pilot plant in Brazil
Petrobras process	Fixed-bed adiabatic reactor	98	A 60-ton/yr prototype plant was operated for a year, a 60,000 ton/yr plant was bought on-stream in 1981; all in Brazil

Part C

Syngas-Based Processes

Syngas-based processes have been very well documented [8]. The gasification of coal or oil provides an alternative route to produce chemicals (Fig. 18). The gasifiers produce CO and H₂ which can be reacted to form a variety of products. Different types of reactions are shown in Table 15. The different operating conditions and different catalyst products produced are shown in Fig. 19.

As shown in Fig. 19, various products may be produced by the conversion of syngas. Most of the reactions are based on F-T (Fisher-Tropsch) technology which was developed almost 60 years ago in Germany. The improved F-T process (SASOL plants) is commercially operated in South Africa. Major products are gasoline and diesel. F-T technology has low selectivity of olefins products. Ethylene is produced as a by-product in SASOL plants. Since 1973, there has been a revival of interest in the F-T process toward producing chemical feedstocks. Modified F-T processes include:

Modified F-T process for olefins production

Modified F-T process for paraffins production as steam cracking feedstock

Upgrade F-T liquids for olefins and aromatics

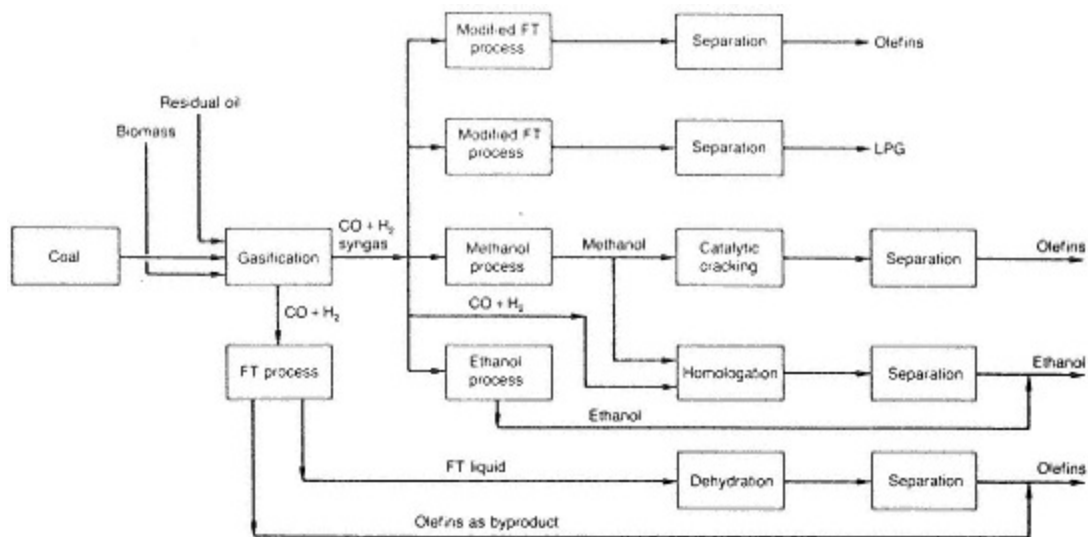


Fig. 18.
Routes to olefins from syngas.

TABLE 15 Possible Stoichiometric Equations for Reactions between Carbon Monoxide and Hydrogen

Methanation	$3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$
	$2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$
	$(2n + 1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
Alkanes ($n > 1$)	$2n\text{CO} + (n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{CO}_2$
	$(3n + 1)\text{CO} + (n + 1)\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n+2} + (2n + 1)\text{CO}_2$
	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
Olefins ($n > 1$)	$2n\text{CO} + n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{CO}_2$
	$3n\text{CO} + n\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n} + 2n\text{CO}_2$
Methanol	$2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH}$
	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n - 1)\text{H}_2\text{O}$
Alcohols ($n > 1$)	$(2n - 1)\text{CO} + (n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n - 1)\text{CO}_2$
	$3n\text{CO} + (n + 1)\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + 2n\text{CO}_2$
Water gas shift	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
Boudouard reaction	$2\text{CO} \rightarrow \text{C} + \text{CO}_2$
Coke deposition	$\text{H}_2 + \text{CO} \rightarrow \text{C} + \text{H}_2\text{O}$
Carbide formation	$x\text{M} + \text{C} \rightarrow \text{M}_x\text{C}$

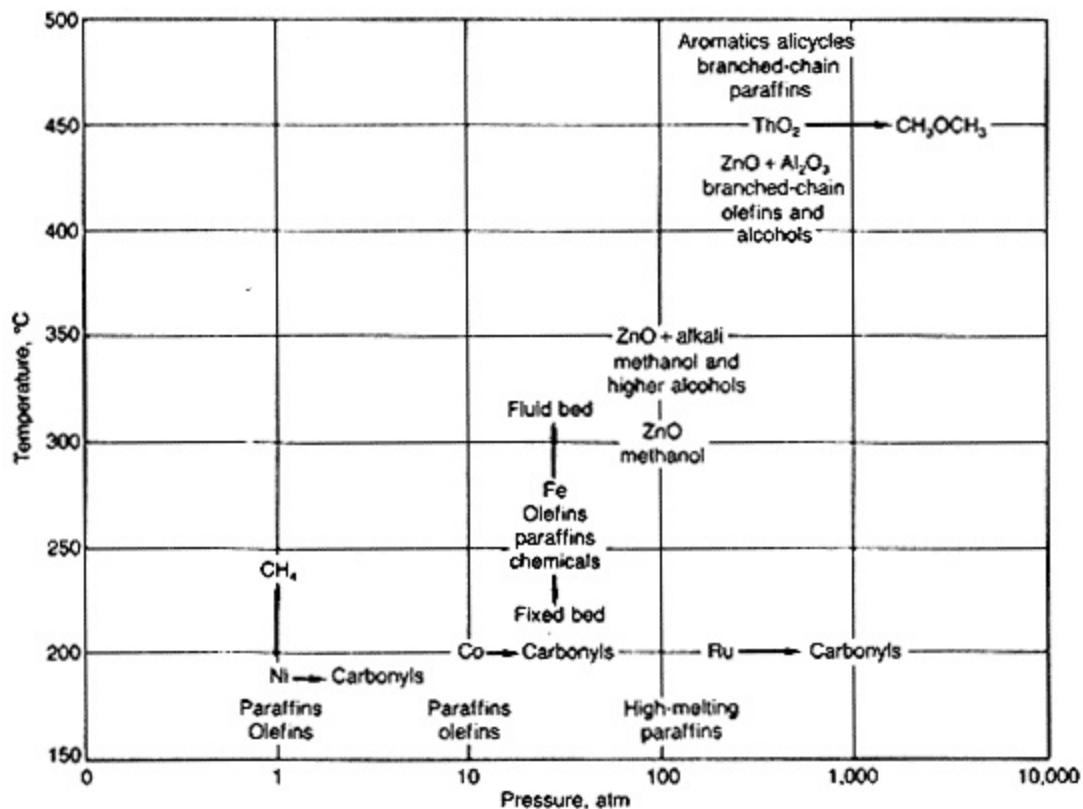


Fig. 19.
Carbon monoxide-hydrogen reactions.

In addition to modified F-T processes, olefins can be produced indirectly from:

- Catalytic conversion of methanol
- Methanol homologation for ethanol and dehydration
- Synthesis of ethanol from syngas and dehydration
- Cracking of carboxylic acid esters

Modified F-T Process for Olefins Production [9]

To improve selectivity of olefins for the F-T process, three approaches are available: changes in operating conditions, changes in reactor design, and development of high selectivity catalysts.

Changes in Operating Conditions

The influence of process variables on the product distribution of the F-T process is shown in Fig. 20. In general, the formation of olefins is followed by low pressure, high space velocity, high temperature, and high CO/H₂ ratio of the syngas.

Changes in Reactor Design

There are three types of reactors: fixed-bed reactor (ARGE reactor) (Fig. 21), entrained-bed reactor (Fig. 22), and slurry-bed reactor (Fig. 23). The first two types have been demonstrated commercially at SASOL's plants, while a slurry-bed reactor pilot plant was demonstrated by Rheinpreussen-Koppers.

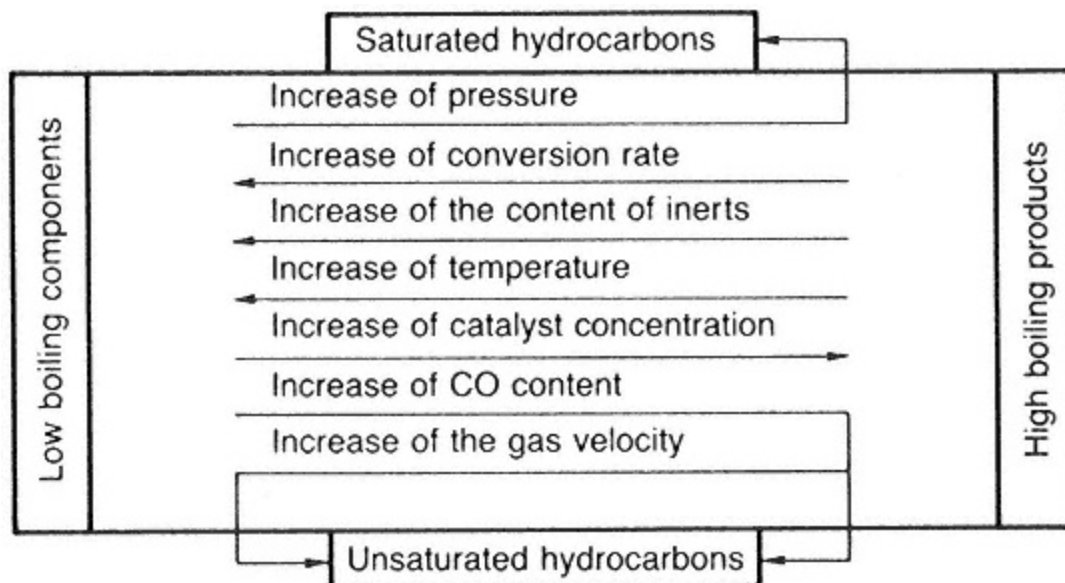


Fig. 20.
Influence of process parameters on the product distribution for the F-T process.

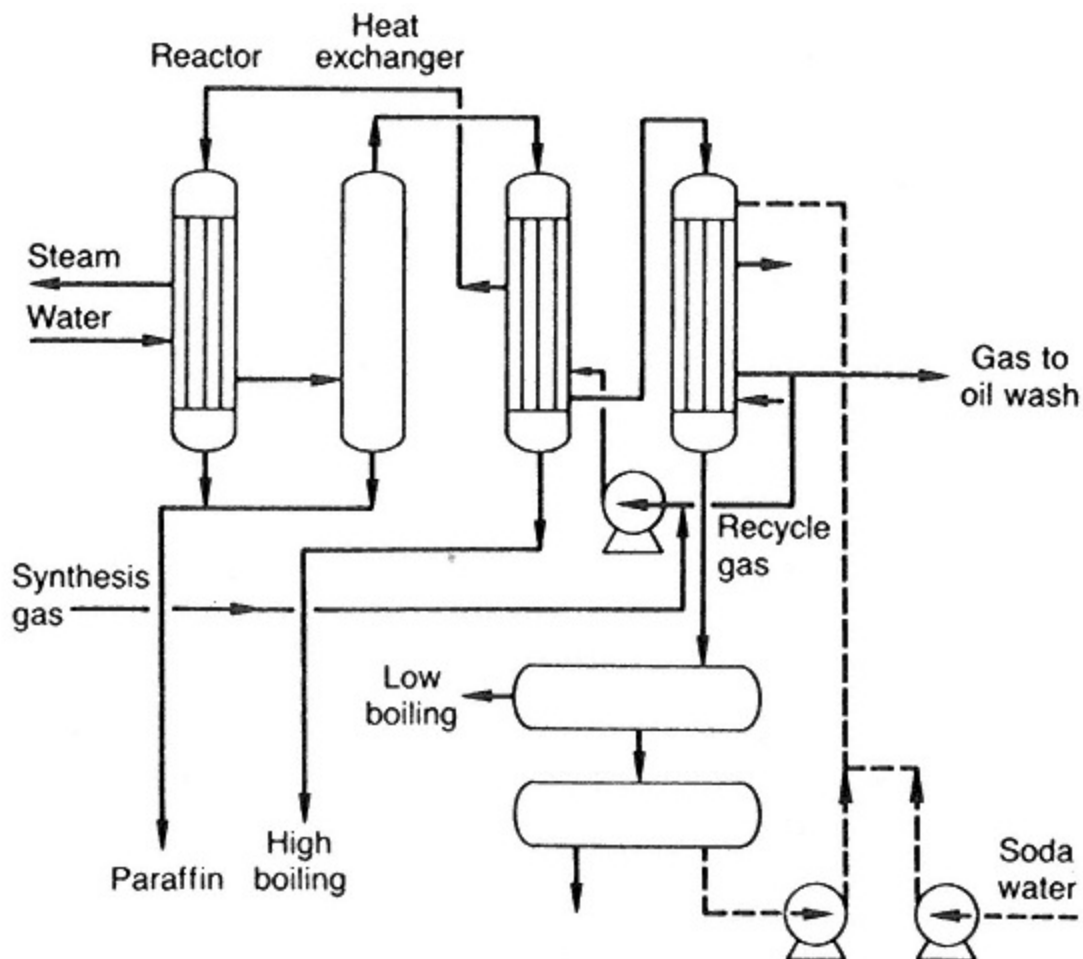


Fig. 21.
The F-T process using ARGE reactor.

Different types of reactors provide different types of heat transfer and different residence time distributions. These in turn cause different product distributions. Table 16 compares the conditions and products for three types of reactors. This indicates that the entrained-bed reactor produces more olefins than the ARGE reactor; the slurry-bed reactor produces more propylene. UOP evaluated four types of reactors: a tube wall reactor system with a

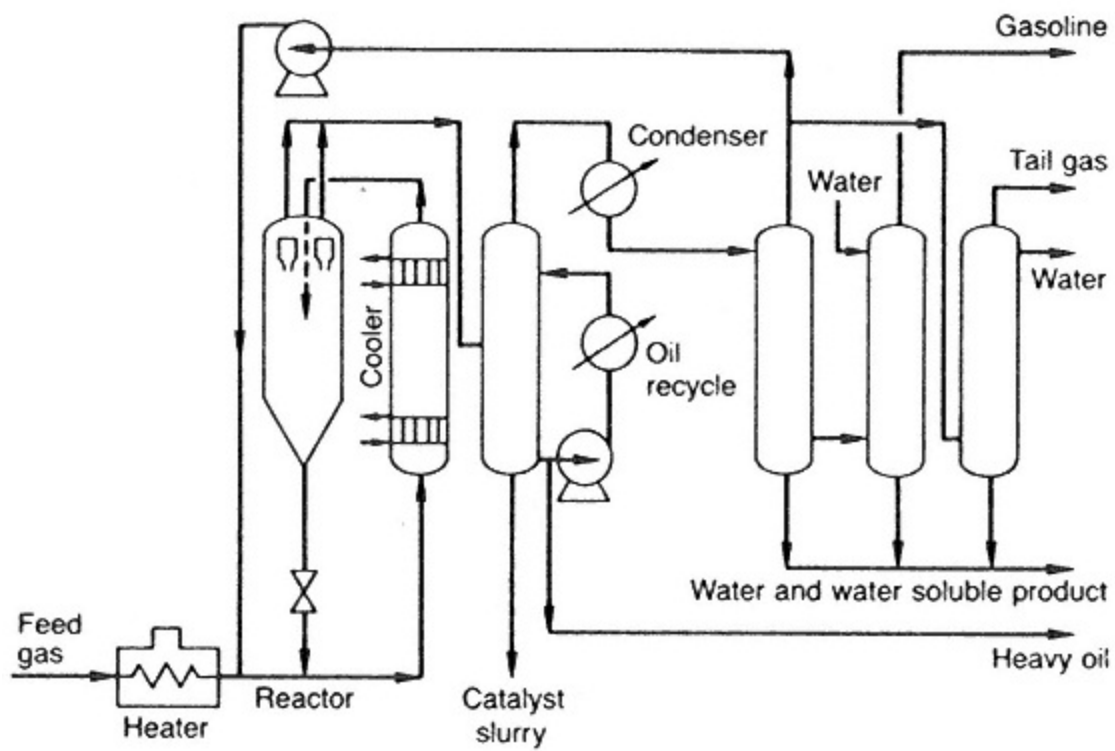


Fig. 22.
The F-T process using entrained-bed reactor.

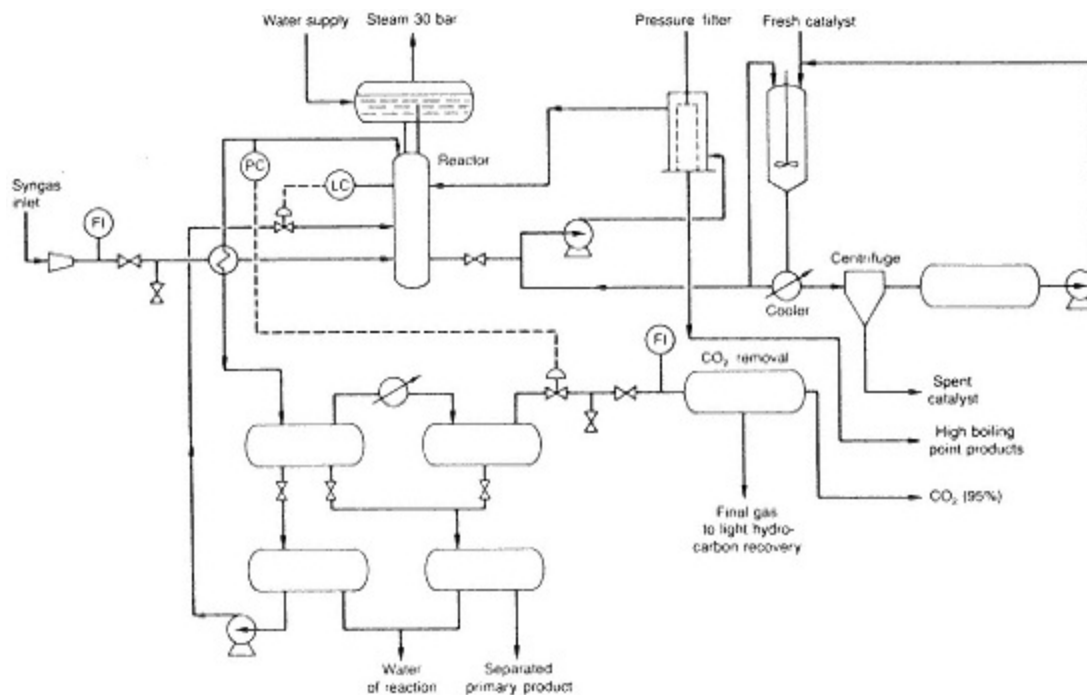


Fig. 23.

The F-T process using slurry-bed reactor.

flamed, sprayed catalyst; a slurry-bed reactor system, an ebullating-bed reactor system, and an entrained-bed reactor system. Investigation suggested that the slurry reactor may be the reactor of choice for low-molecular-weight olefins.

TABLE 16 Comparison of Performance for Three Types of F-T Reactors

	ARGE Sasol 1	Entrained Fluidized Sasol 1	Slurry Reactor Rheinpreussen- Koppers
Temperature, °C	220250	300350	260300
Pressure, bar	2325	2023	12
Ratio CO/H (feed)	0.50.8	0.360.42	1.5
Wt.% C ₂ C ₄ :			
C ₂ H ₄	0.1	4.0	3.6
C ₂ H ₆	1.8	4.0	2.2
C ₃ H ₄	2.7	12.0	16.95
C ₃ H ₈	1.7	2.0	5.65
C ₄ H ₈	2.8	9.0	3.57
C ₄ H ₁₀	1.7	2.0	1.53
Total: C ₂ C ₄ olefins	5.6	25.0	24.12
C ₂ C ₄ paraffins	5.2	8.0	9.38

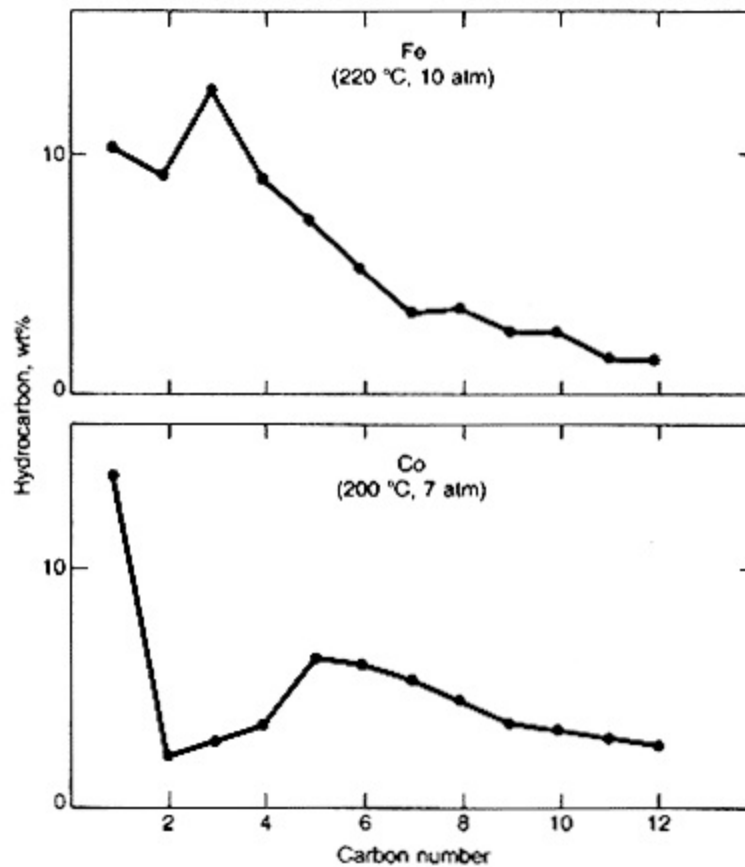


Fig. 24.
Molecular weight distribution of hydrocarbon products in medium pressure F-T process.

Development of High Selectivity Catalysis

Conventional F-T catalysts are iron catalysts and cobalt catalysts which produce a wide spectrum of hydrocarbons (Fig. 24).

An ideal selective catalyst compared to iron and cobalt catalysts is shown in Fig. 25.

In order to develop a selective catalyst, several approaches have been adapted.

Metals Encapsulated in Zeolites

Various kinetic models were proposed for F-T reactions. Three major reaction mechanisms have been considered:

Chain growth by condensation

Chain growth by insertion of CO into the metalhydrocarbon bond

Chain growth by polymerization of methylene groups

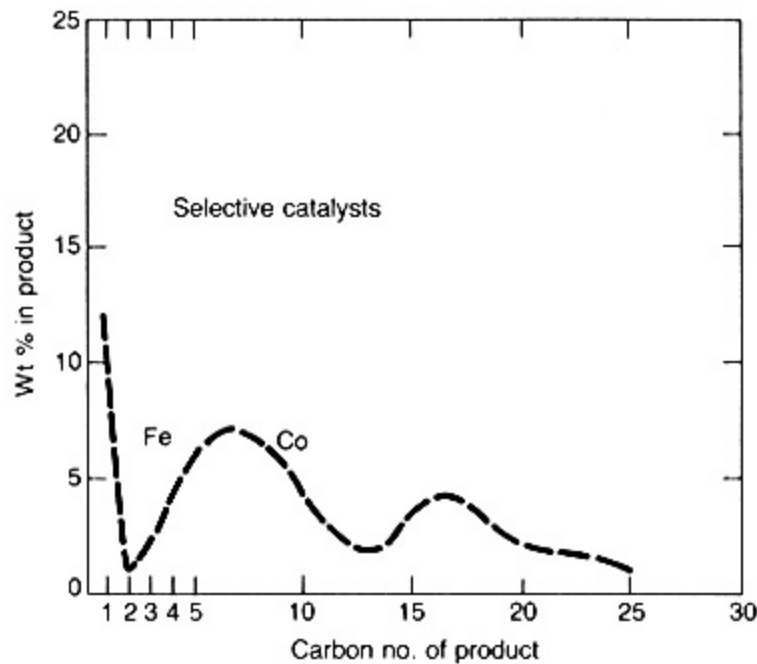


Fig. 25.
Distribution of the synthesis properties of iron and cobalt catalysts
and selective catalysts.

In principle, the normal chain-growth process can be terminated by physical constraints imposed by containment of the catalyst in small pores. Several examples of this approach have been reported for F-T catalysts contained in zeolites and on aluminas of various pore sizes. Limitations on chain growth for metals encapsulated in zeolites have been reported for Co-A, Co-Y, and Ru-Y catalysts. With Co-A, only propylene was produced from COH_2 at 151°C and 6 atm total pressure.

In addition to pore size, the acidity of zeolites is also important for the types of hydrocarbons produced. If silicalite is used instead of ZSM-5 (high acidity) as the catalyst support, the product stream is rich in olefins instead of aromatics.

Two-Stages Catalysts

In this approach, low molecular weight intermediates derived from a COH_2 synthesis reactor are intercepted before the normal polymerization process occurs. An example of this approach is Mobil's research concerning the synthesis of light hydrocarbons directly from synthesis gas using a bifunctional catalyst. One function produces an alcohol or hydrocarbon intermediate; the other function converts the intermediate into light hydrocarbons including olefins.

Chemical Modification of Iron Catalysts

Many modified iron catalysts have been reported during the past several years.

Iron catalysts modified by oxides of titanium, vanadium, molybdenum, tungsten, and manganese

Selectivity of the catalysts is obtained by partially poisoning the catalysts with sulfur, such as partially poisoned iron whiskers with the addition of promoters

Pure electrolytic manganese alloying with 10-20% iron. The composition of these products can be influenced by varying the Mn-Fe ratio over a wide range

Iron catalysts with an oxide of cobalt

Iron catalysts with potassium

Iron catalysts with manganese and calcium

Carbon-supported iron catalysts

Other Catalysts

Cobalt-based catalysts include:

Cobalt-copper with Al_2O_3 support

Chromium and zirconium doped cobalt catalysts

Ruthenium-based catalysts include:

Ruthenium supported on manganese oxide, titanium oxide, and alumina oxide, modified by strong metal-support interactions

Ruthenium-iron catalysts

Rhodium catalysts containing alkali metal promoters

The revival of interest in syngas reactions is a new frontier for catalyst chemistry. Various activities on high C_2C_4 selectivity F-T catalyst development are in progress in both industry and academia, but it is too early to draw conclusions. Table 17 compares some high selectivity catalysts.

Modified F-T Process for Steam Cracking Feedstock

A new supported and promoted molybdenum catalyst has been developed by Dow Co. to convert more than 70% syngas to LPG (C_2C_5) material. The supporting materials are carbon or alumina, and the promoters are alkali

TABLE 17 Comparison of High Selectivity Catalysts for Modified F-T Process

	Silicalite with 7.8% Fe, 0.9% K	Precipitated Fe-Mn	100 Fe:100 Mn:10 ZnO:4 K ₂ O	Ru/MnO
Temperature, °C	280	290	320	350
Pressure	21 bar	14 bar	10 atm	103 kPa
H ₂ /CO ratio	0.9	0.8	1.0	0.5
Space velocity (h ⁻¹)	1300	353	500	350
C ₂ C ₄ compounds, wt. %:				
C ₂ H ₄	8.2	7.6	31.3	30.0
C ₂ H ₆	0.4	4.9		8.0
C ₃ H ₆	19.3	17.3	22.2	32.0
C ₃ H ₈	0.2	2.1		1.0
C ₄ H ₈	8.6	15.2	17.4	7.5
C ₄ H ₁₀	0.2	3.1		0.5
C ₂ C ₄ olefins	36.1	40.1	70.9	69.5
C ₂ C ₄ paraffins	0.8	10.1	15.7	9.5
Total C ₂ C ₄	36.9	50.2	86.6	79.0

TABLE 18 Selectivity of C2C5 Paraffins for Molybdenum Catalysts

	Mo Catalyst, No Alkali, Bureau of Mines	Mo Catalyst with Alkali, Dow
Temperature, °C	400	400
Pressure, lb/in. ²	900	900
H ₂ /CO ratio	1	1
Space velocity, HSV	300	300
% carbon selectivity in hydrocarbon product:		
C ₂	20.4	30.0
C ₃	7.8	19.5
C ₄	1.8	7.3
C ₅		3.7
C ₂ C ₅	30.0	62.3

metals. The principle components for the LPG produced are ethane and propane (31 and 21%, respectively). High yields of ethane and propane are particularly desirable because they crack most efficiently to ethylene. The moly catalysts also have a high tolerance for sulfur. Because of the catalysts low rate of coking, high reactor temperatures are possible. High reactor temperature allows for high conversion. Selectivity for molybdenum catalysts are shown in Table 18. For alkane production, Texaco developed catalysts by reducing and chloriding ground magnetite of specific particle size.

During Dow's scale-up of the PCC process for cracking whole crude and/or heavy resid to ethylene, a sizable by-product of clean H₂/CO was a coproduct. Dow developed a ruthenium catalyst [10, 18] to convert H₂/CO into LPG. This process can be used to produce feedstock for the ethylene cracking furnace.

Shell International Petroleum Maats-Chappij also developed a process (SMDS process) [11] to produce middle distillate from H₂/CO gas. Because the distillate is paraffinic, it makes an excellent cracking feedstock.

Catalytic Conversion of Methanol [12, 13]

The synthesis of hydrocarbons from methanol using the Mobil MTG Process with ZSM-5 catalyst is shown in Fig. 26.

Paraffins, olefins, and aromatics can be produced from syngas indirectly through methanol. By controlling structural and process parameters, the production of olefins or aromatics can be enhanced. This is shown in Fig. 27.

The exact reaction pathway for olefins formation from methanol cracking is being elucidated. However, a simplified hypothesis can be assumed as follows:

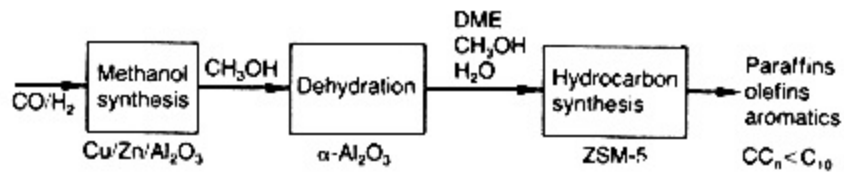
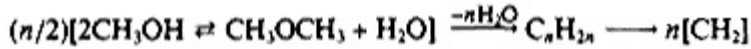


Fig. 26.

Mobil methanol to hydrocarbons technology.



where $[\text{CH}_2]$ = average formula of aromatic-paraffin mixture.

Olefins are intermediates in the conversion of methanol to aromatic hydrocarbons over zeolite. In order to increase olefins production, conditions under which the final aromatization step is minimized or suppressed must be found.

Various approaches to this problem have been developed. The simplest strategy is to backtrack along the reaction path by decreasing the contact time. Here, maximum olefins selectivity may be obtainable only at partial conversion, which requires separation and recycling of unreacted material. Decoupling of olefins from aromatics formation can be achieved by reducing the oxygenate partial pressure. At low partial pressure, generally below atmospheric, this method provides high olefin yields at complete conversion.

Improvement in olefin selectivity through ZSM-5 modifications using P, Mg, and silanes has been reported.

Small pore zeolites which cannot sorb, such as erionite and chabazite, produce light olefins from methanol.

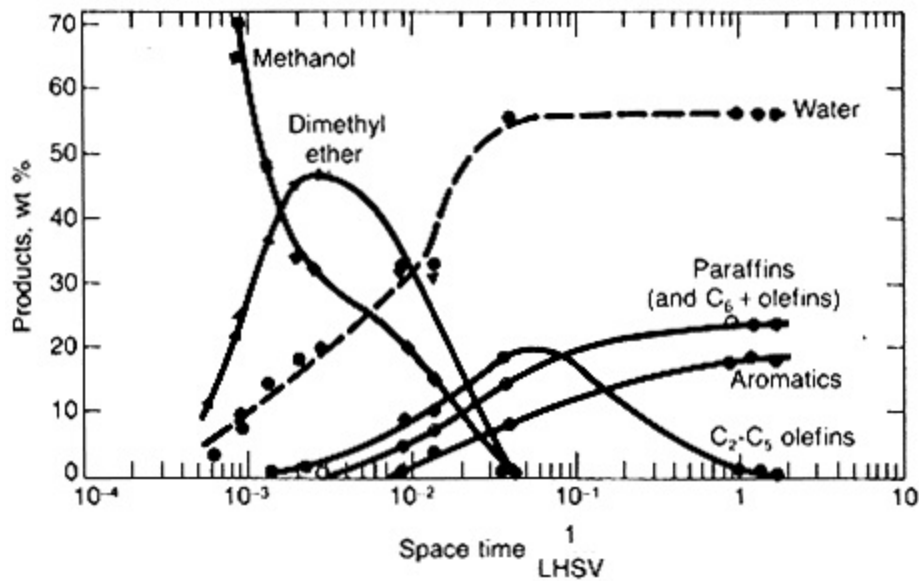


Fig. 27.

Controlling the reaction can encourage the production of olefins.

Olefins can also be decoupled from aromatization via a combination of high temperature and catalyst activity ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio). Selectivity to olefins can be enhanced by a cooperative effect of increased temperature and increased catalyst $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The selectivity enhancement is due to decoupling of olefin formation from aromatization, brought about by differences in the activation energy and acid dependency of the two reactions. For ZSM-5-type catalyst the propylene exceeds ethylene by a factor of 5 or more (on a weight basis). In a partial conversion, the process in the presence of water can produce as much as 28% ethylene, with ethylene exceeding propylene by a factor of almost 2.

The early reported catalysts for methanol conversion to ethylene are:

Aluminasilicate zeolite (Mobil Oil)

Aluminum silicate containing manganese (Hoechst AG)

Small pore catalysts such as chabazite ion exchanged with a mixture of rare earth chlorides (Texas A&M)

Modified H-ZMS-5 with phosphorus (Mobil Oil).

The performance of these catalysts is shown in Table 19.

Two major types of zeolite used for methanol conversion to ethylene exist: small pore zeolites such as ZSM-34, and large pore zeolites such as ZSM-5. With ZSM-34, ethylene selectivity can be 50%, but catalyst life is short due to blockage of the core by carbon deposits. ZSM-5 has a long catalyst life, but ethylene selectivity is low (6.4 wt.% at 450°C).

Two improved catalysts were developed at Kyoto University [15, 16]. Type-I was similar to ZSM-34 and Type-II was similar to ZSM-5. Conversion data for Type-I and Type-II are shown in Table 20.

Metallosilicates with the pentasil pore opening structure have been proposed as catalysts for olefin synthesis with high selectivity and long catalyst life. A novel Fe-silicate catalyst was developed at Kyoto University [17]. Selectivity to C_2C_5 olefins was achieved as high as 97.6 C-mol.%, and the space-time yield reached 11.9 C-mol/L·h at 295°C.

Since carbon deposits on catalysts are critical, Mobil [14] developed a fluidized-bed process for the production of olefins from methanol. The process is based on the ZSM-5 family of shape-selective zeolite catalysts. Initial development in fixed- and fluid-bed micro-units gave total olefin selectivities exceeding 75 wt.% of hydrocarbons with complete methanol conversion. A scale-up to a 4-BPD fluid-bed pilot plant was successful in maintaining high olefin yield. The process has recently been scaled up in a 100-BPD demonstration plant in Germany.

Le Van Mao and coworkers [31] at Concordia University, Montreal, developed catalysts with Zn and Mn loaded on ZSM-5 zeolite-asbestos. The light olefins/aromatics ratio in the

products varied with the Mn content in the catalyst. The Zn-Mn loaded zeolite catalysts exhibited a high methanol conversion into hydrocarbons.

TABLE 19 Comparison of Catalysts for Methanol Conversion to Olefins

	13x Molecular Sieve Plus Manganese (Hoechst)	Chabazite Ion Exchanged with a Mixture of Rare Earth Chlorides (Texas A&M)	Phosphorus-Containing Zeolite (Mobil)	Aluminosilicate Zeolite (ZSM-5)
Temperature, °C	150	416	370	370
Pressure	1 bar	1 bar		2 atm
Feed	Methanol	Methanol plus CS ₂	Methanol	Methanol
Conversion	90.1	90.0		
C ₂ -C ₄ wt.% in hydrocarbons:				
C ₂ H ₄	46.9	35.0	37.5	
C ₂ H ₆	3.7	11.0	0.0	
C ₃ H ₆	29.2	23.0	28.0	
C ₃ H ₈	0.5	22.0	0.0	
C ₄ H ₈	5.3		4.2	
C ₄ H ₁₀	2.1		3.9	
Total: C ₂ -C ₄ olefins	81.4	26.5	39.7	
C ₂ -C ₄ paraffins	6.3	33.0	3.9	

TABLE 20 Methanol Conversion Data for Type-I, Type-II, and Reference Catalysts

	Type-I Zeolite	ZSM-34	Type-II Zeolite	ZSM-5
Temperature, °C	400	400	300	400
MeOH concentration, % ^a	12	12	20	20
LHSV of MeOH, h ⁻¹	0.126	0.126	1.443	0.360
GHSV of gas mixture, h ⁻¹	1000	1000	4000	1000
MeOH conversion, %	100	100	75.7	72.8
MeOH conversion to hydrocarbons, %	100	100	12.6	55.5
Space-time yield (C-mol/L · h)	5.36	5.36	4.48	8.93
Hydrocarbon distribution, mol.%:				
CH ₄	7.9	21.3	23	1.6
C ₂ H ₄	23.5	32.4	41.1	9.1
C ₂ H ₆	0.0	0.0	0.0	0.7
C ₃ H ₆	23.6	20.5	39.8	9.9
C ₃ H ₈	1.1	9.9	1.1	16.3
C ₄ H ₈	23.6	11.0	5.4	7.0
C ₄ H ₁₀	1.1	4.9	4.9	24.1
C ₅ +	8.6	0.0	5.4	31.3
C ₂ -C ₄ olefins (mol.%)	81.3	63.9	86.3	26.0
C ₂ -C ₄ olefins (C-wt.%)	80.6	70.7	81.3	17.8

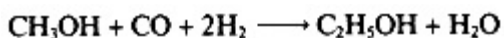
^aUse nitrogen as the diluent.

Upgrade F-T Liquids to Olefins and Aromatics

The F-T process produces large quantities of liquid oxygenates. These include methanol, ethanol, propanol, higher alcohols, and aldehydes. H-ZSM-5, a shape-selective zeolite, has been utilized to convert oxygenates into hydrocarbons. High yields of hydrocarbons include ethylene, propylene, C₄-C₈ olefins, and aromatics. This is essentially an extension of the technology of methanol conversion to olefins.

Ethanol Via Homologation and Dehydration to Olefins

The reaction of methanol with synthetic gas to produce ethanol was discovered by workers in the U.S. Bureau of Mine in the 1950s:



The reaction was catalyzed by cobalt carbon, and yields were low (42%) with a spectrum of by-products. The homologation reaction has recently been reinvestigated, and the selectivity of ethanol has been increased to 90%, but with a low reaction rate. Gulf Oil's homogeneous catalyst for homologation contains ruthenium and iodide ions and may contain phosphorous ligands. British Petroleum utilizes catalysts containing cobalt, an iodide or a bromide, and a polydentate ligand. Union Carbide also studied a phosphineiodine promoted cobalt-ruthenium catalyst. Rhone-Poulenc tested catalysts in the presence of cobalt, ruthenium, ionic halide, and alkyl halide in specific ratios.

For the Gulf process the reaction is carried out at 175°C and 4000 lb/in.² in the presence of a catalyst consisting of a cobalt-ruthenium complex, a trialkyl phosphine ligand, and an iodine promoter.

Methanol conversion is 30% with a residence time of 1 h. Selectivity can be as high as 96%.

Ethanol can be dehydrated to olefins as discussed in Part B.

Ethanol Via Syngas Synthesis and Dehydration to Olefins

Catalysts containing rhodium can produce a range of C₁ to C₄ linear alcohols with an ethanol content of 40-60%. Of special interest is the product spectrum obtained with a cobalt-copper-chromium-potassium catalyst, which consists of methanol, ethanol, n-propanol, and n-butanol in a by-weight proportion of 0.61, 1.00, 0.56, and 0.44. Sagami Chemicals developed a catalyst using rhodium on a metal oxide. Hoechst has cobalt catalysts promoted with gold, silver, and/or ruthenium; 50-65% selectivity for ethanol is claimed. Union Carbide also studied rhodium-based catalysts. Phillips studied cobalt carbonyl catalysts with phosphines as promoters for use at high pressure (38,000 lb/in.² gauge); alcohol selectivity is 35%, with 31% methanol and 17% ethylene glycol as by-products.

Ethanol can be dehydrated to olefins as discussed in Part B.

Cracking of Carboxylic Acid Esters/Texaco [19]

A two-step process scheme for the production of ethylene from synthesis gas has been proposed. The first stage involves hydrogenation of carbon monoxide to ethyl ester in the presence of an aliphatic carboxylic acid. The catalysts are homogeneous ruthenium catalysts coupled with quaternary phosphonium salt promoters. During the second stage the isolated, intermediate ethyl ester may be either pyrolyzed to yield ethylene or hydrolyzed to yield ethanol. The by-product acid is recycled as the cocatalyst (Fig. 28).

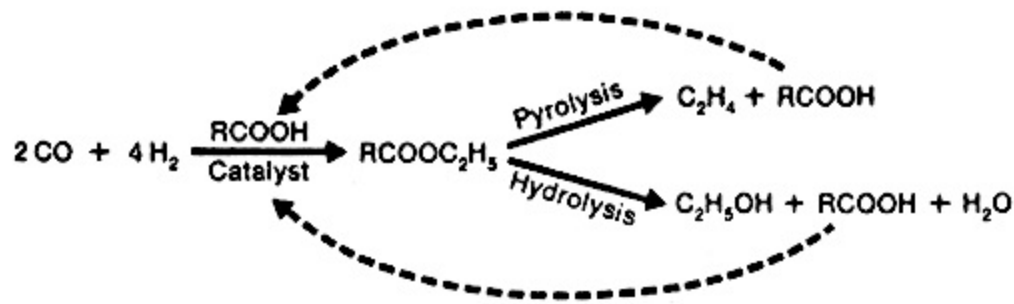


Fig. 28.

Ethylene process uses ruthenium catalyst.

Syngas has one major advantage over petroleum-based chemical feedstocks; it can be produced from many sources, such as light or heavy oil fractions, coal, natural gas, or even wood and municipal wastes. The new surge of C1 chemistry research leaves no doubt that technological improvements in various areas of syngas-based olefins processes are possible.

Part D

Dehydrogenation of Paraffins

Several processes have been developed to dehydrogenate paraffins (ethane, propane, butane, or mixtures) into olefins. These are the CATFIN process, STAR process, Oleflex process, and Ethoxene process. The first three processes are used for processing C3 and C4 paraffins. The Ethoxene process is used for C2 paraffin.

Air Products/CATFIN Process (Fig. 29) [20]

Paraffins are preheated by heat exchange with the reactor effluent, and in a fired heater this is done prior to contact with the catalyst. Pressure in the reactor is selected to optimize the relationship between selectivity and energy consumption. In a given reactor, the on-stream period is followed in turn by steam purge, evacuation, preheating with air (concurrently with decoking), and evacuation. The reactor is then returned to processing. Multiple reactor systems are used to provide continuous flow.

Major operating conditions for the reactor are as follows:

Temperature, °F	10001400
Pressure, Hg abs	1020
Space velocity, v/h/v	<1

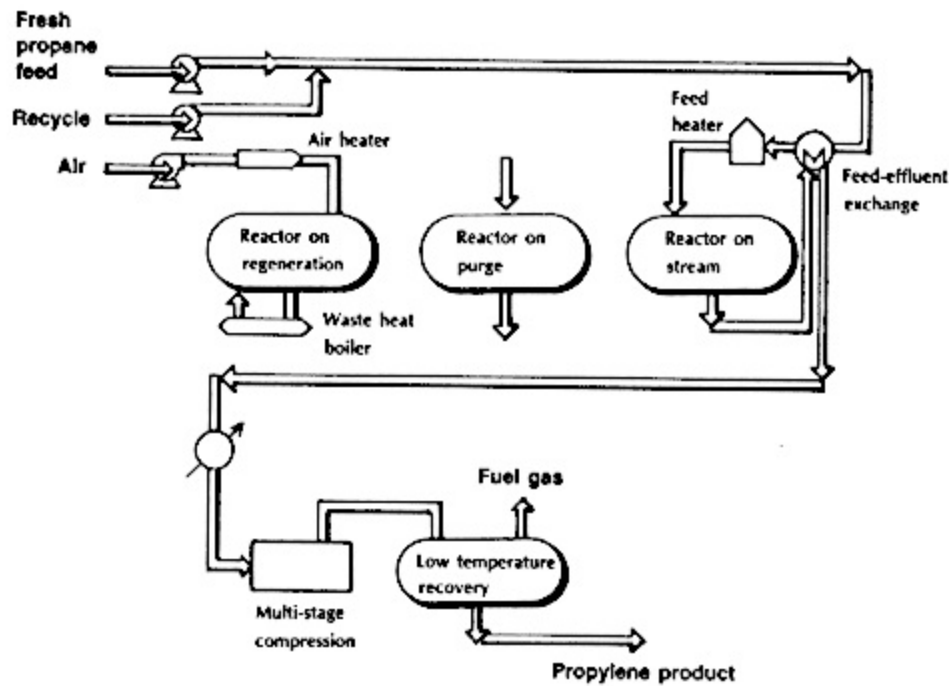


Fig. 29.

CATFIN process.

Source: Air Products & Chemicals Inc

The catalyst is in the form of cylindrical pellets consisting of chromic oxide on an active alumina support. The required reaction heat is supplied by storing heat in the catalyst bed during the decoking step. The dehydrogenation reaction uses this heat during the reactors' on-stream period. When making butylene or propylene, ultimate yields of olefin from paraffin will be 75 to 90 wt.%.

Phillips/STAR Process (Fig. 30) [21]

This process can perform dehydrogenation and/or dehydrocyclization of paraffinic feedstocks. Light paraffins can be dehydrogenated to their respective monoolefins with selectivities as high as 95%. The catalyst for the STAR process has a unique neutral base. Multiple metal promoters are used to provide and sustain activity. Since the base is neutral, acidic-promoted structural isomerization is minimized. This contributes to high selectivities. The catalyst has a useful life of at least 1 year and is air-regenerated. The reactions are equilibrium limited and are favored by high temperature and low pressure. Steam used in the STAR process serves as a diluent to favor the dehydrogenation equilibrium.

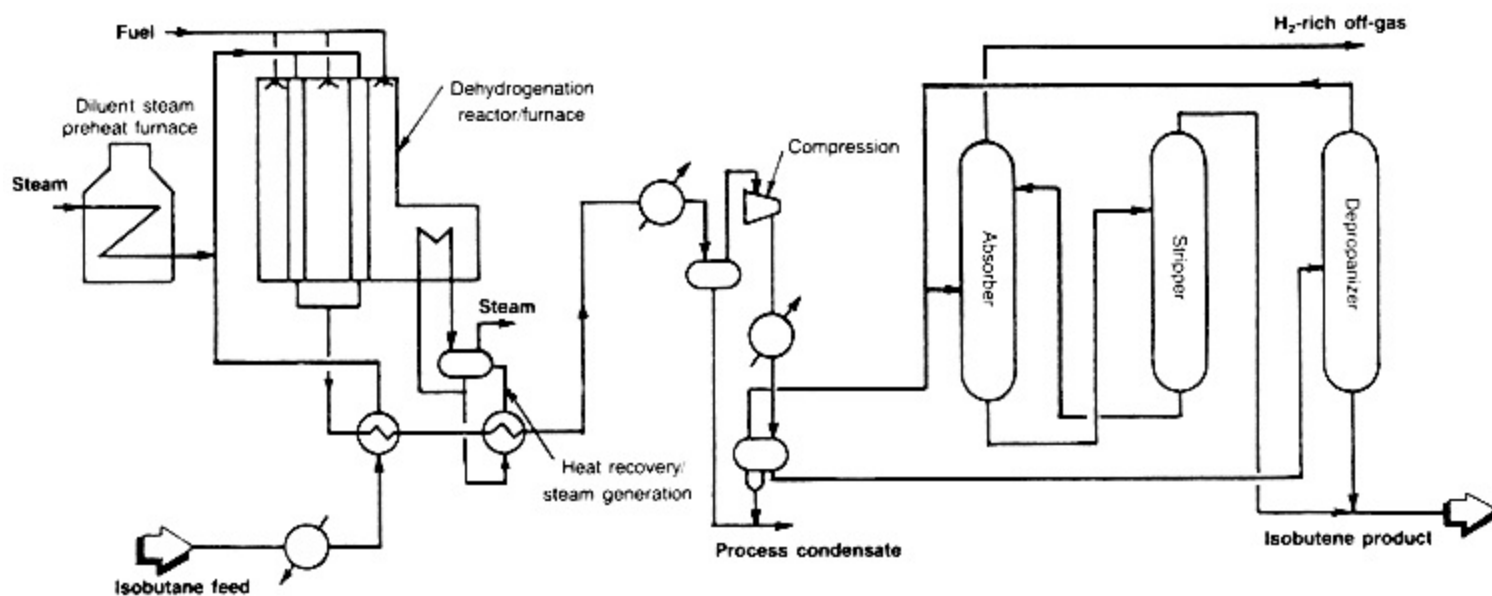


Fig. 30.
STAR flow scheme.

TABLE 21 Propane Dehydrogenation

Temperature, °F	1050	1100	1150
Conversion, %	28.4	35.2	39.4
Selectivity, %:			
Olefins	94.6	93.0	88.6
Gas	3.9	4.6	7.0
Carbon oxide	1.4	2.4	4.4

The process is operable over a wide range of conditions, tailored to the individual feedstocks. The use of moderate pressures, generally 30 to 100 lb/in.² gauge, minimizes the need for compression prior to product purification. The temperature is maintained above 900°F. The propane dehydrogenation performance is shown in Table 21.

UOP/Oleflex Process [22]

A typical flow sheet is shown in Fig. 31.

The reaction stages are stacked on top of one another. Each stage is a radial flow reactor. The annuli filled with catalyst are interconnected in such a way that small, discrete amounts of catalyst can be continually withdrawn from the bottom of the stack and sent to regeneration. At the same time, an equivalent amount of regenerated catalyst is added back at the top. The continuous catalyst regeneration section is shown in Fig. 32.

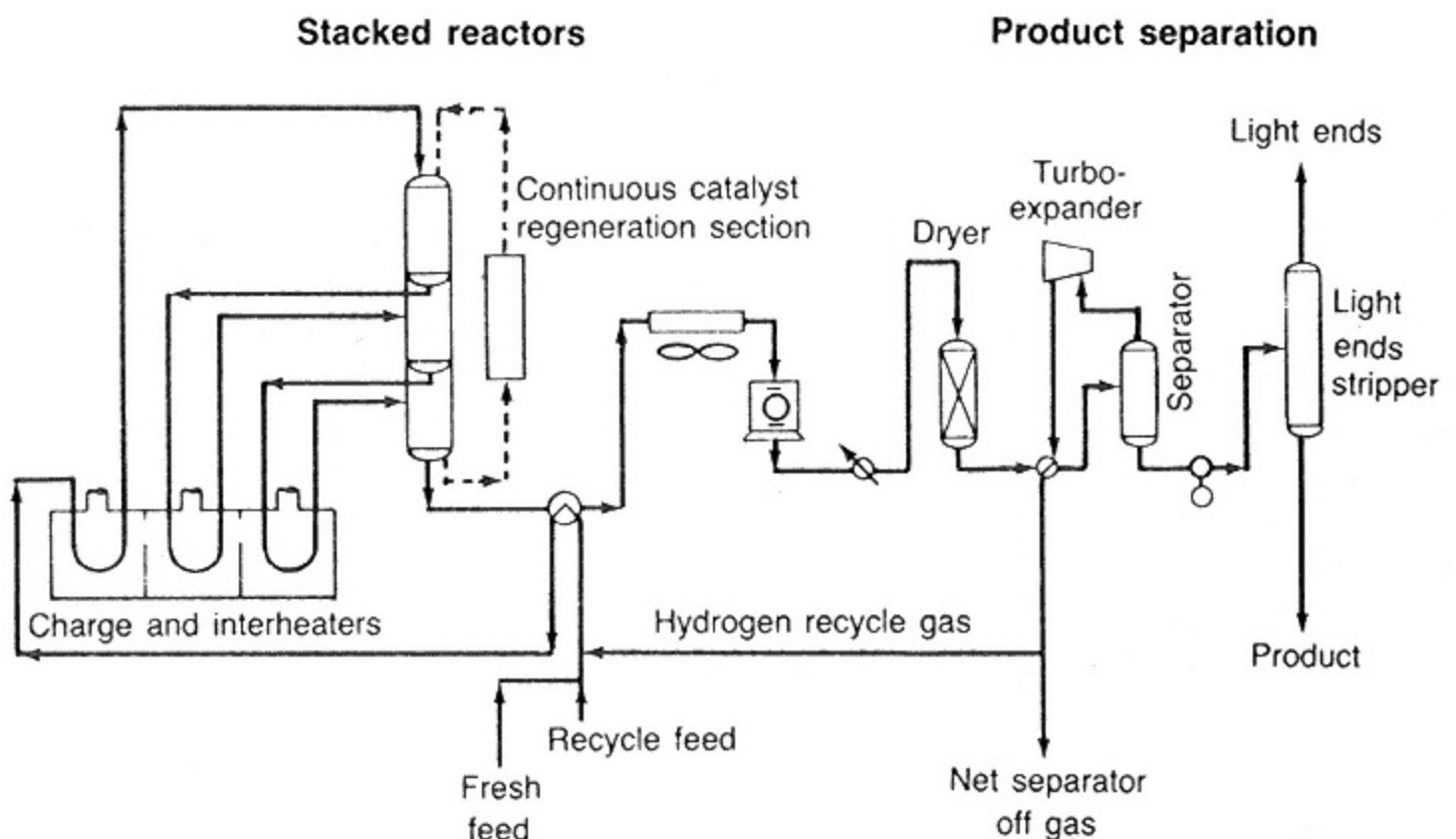


Fig. 31.
Oleflex process.

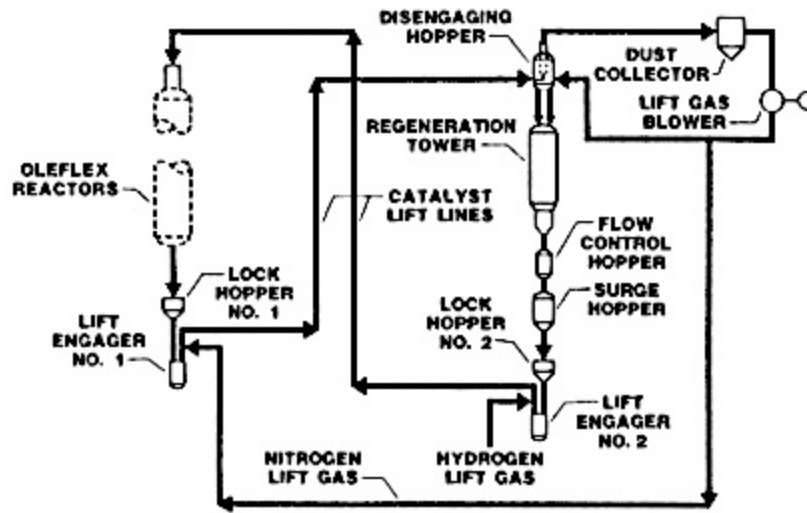


Fig. 32.

UOP continuous catalyst regeneration section. The Oleflex regeneration section is identical to the platforming regeneration section.

In the reactor circuit, fresh feed is mixed with unconverted hydrocarbon recycle feed and hydrogen-rich recycle gas and heated to the desired reactor inlet temperature. This mixed feed is converted to monoolefins in a series of stacked reactors. Since the reaction is endothermic, conversion is maintained by supplying heat, equivalent to the heat of reaction, through interstage heaters.

The effluent gas exits the last reactor and exchanges heat with the combined feed. A series of exchange, compression, and turbo expansion or other recovery system is used to separate the relevant C₃ or C₄ hydrocarbons as a liquid from the combination of the recycle gas and the hydrogen-rich off-gas. The high purity (approximately 90 mol%) of the hydrogen-rich off-gas makes it a valuable product.

Liquid from the separator is pumped to a light ends stripper where components lighter than C₃ or C₄ are removed overhead. The bottoms from the stripper consist of the desired monoolefins product and the unconverted paraffin feed.

Depending on the type of feedstocks, the selectivity varies between 80 and 90 mol%, and yield varies between 81 and 92%.

Union Carbide/Ethoxene Process [23]

This process utilizes a proprietary catalyst for the oxidative dehydrogenation of ethane to produce ethylene at a temperature of 300-400°C (572-752°F)

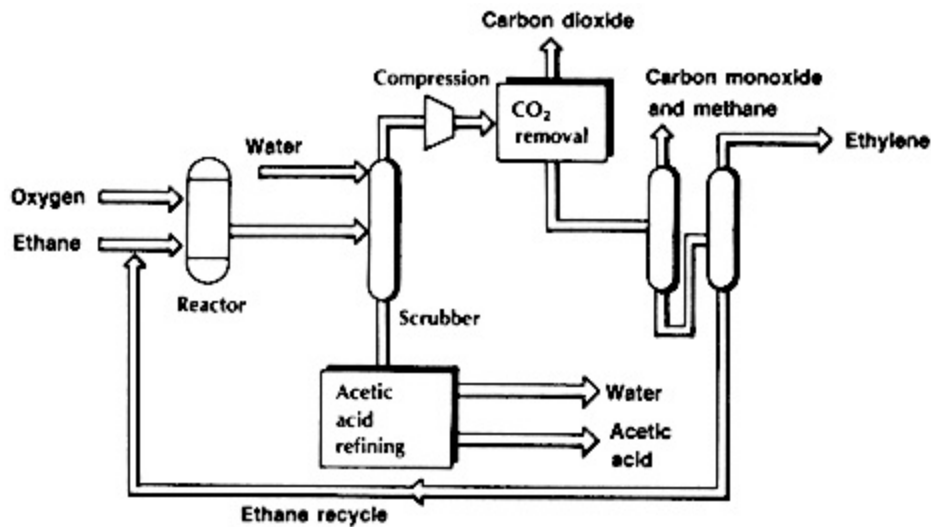


Fig. 33.
Carbide's Ethoxene process.

over a pressure range of 1 to 40 atm in the gas phase. There is little cracking under these conditions. By-products are few, only acetic acid, water, and very small quantities of carbon dioxide and carbon monoxide. The efficiency of converting ethane to ethylene and acetic acid is as high as 90%. The ratio of ethylene to acid can be altered within wide limits, up to 10:1.

The flow sheet is shown in Fig. 33.

Pipeline quality ethane reacts with oxygen, supplied either by pipeline or from a dedicated air separation unit. Besides ethylene and acetic acid, small quantities of carbon dioxide and carbon monoxide are formed. Scrubbing removes acetic acid from the reactor effluent; refined acetic acid may be produced in a conventional extraction and azotropic distillation system.

The ethylene-containing gases from the scrubber overhead are fed to a conventional alkanolamine-carbon dioxide removal unit. Following acid-gas removal, the carbon monoxide, methane, and any other light gas are separated from the ethylene and unreacted ethane in a light ends removal unit. Ethylene is separated from ethane in another column to produce high purity ethylene. Ethane is recycled to the reactor.

The advantage of paraffins dehydrogenation over conventional cracking is that the former has higher selectivity than the latter. The Oleflex process seems to have a more sophisticated system than the CATFIN and STAR processes.

The economics of the Ethoxene process depend on the utilization of by-product acetic acid. Overall, paraffins dehydrogenation processes can be used to balance the product distribution of a petrochemical complex.

Part E

Other Processes

Oxidative Coupling of Methane

Oxidative coupling of methane to produce C₂ compounds has received some recent attention [24]. The processes include pyrolytic and catalytic types.

Pyrolytic Process [25]

Professor S. Benson of the University of Southern California developed a process that uses two separate reactors. In the first, methane and chlorine are burned in an oxygen-free flame at approximately 1000°C and 1020 atm pressure, producing the chloromethane. The residence time is in the range of 10 to 80 ms. Two chloromethane molecules react to give ethylene, benzene, some acetylene, and two more molecules of hydrochloric acid. In the second step the hydrocarbons are separated from the hydrochloric acid. The hydrochloric acid is burned with oxygen to regenerate chlorine, which is recycled, with any unreacted methane, to the first reactor. The net reaction is two molecules of methane plus one molecule of oxygen to yield one molecule of ethylene plus two molecules of water.

Operating conditions can be varied so that ethylene is the primary product at high temperature and a CH₄:Cl₂ ratio of less than 2:1. At low temperature and a high CH₄:Cl₂ ratio, ethane is produced to the substantial exclusion of ethylene.

KTI designed a bench-scale pilot plant for this process and carried out tests at Battelle Northwest. One of the primary objectives of future work will be to arrive at a system which can economically recover chlorine and accommodate or combat high corrosion.

Catalytic Processes

Texas A&M Process [26]

Recent work at Texas A&M has demonstrated that lithium-doped magnesium oxide (Li/MgO) in the presence of O₂ has high activity for abstracting H from CH₄ to form CH₃ radicals, which in turn produce ethane and ethylene with CO and CO₂ as by-products. At a reaction temperature of 720°C, the conversion of methane was 37.8% with a selectivity to ethane and ethylene of just over 50%.

Phillips Process [27]

Magnesium and calcium oxides promoted with small amounts of lithium, sodium, or potassium have been shown to be very active and selective for the production of ethylene and ethane from methane. Typical methane conversions are 20 to 30% at a net selectivity to C₂'s of better than 60%. Small amounts of C₃ and C₄ hydrocarbons are also produced, with the remaining products being CO₂ and CO. Temperature studies indicate that carbon oxide selectivity drops as the temperature is increased from 600 to 730°C, then rises again as the temperature is further increased. The mechanism appears to be the activation of methane at the catalyst surface with a subsequent release of methyl radicals into the gas phase. Methyl radicals then combine or react with other hydrocarbons. The catalyst operates continuously, requiring no regeneration nor special pretreatment, and appears to be long-lived.

ARCO Process [24]

Researchers at ARCO have recently patented a series of supported metal oxides that are very effective for the conversion of methane into ethane and ethylene. These catalysts are based on reducible metal oxides and are used in a stoichiometric fashion by alternately exposing them to an oxidizing atmosphere and then to methane in the absence of oxygen.

Most of the work reported has low methane conversion and low stability. More recently, ARCO has been able to improve and stabilize methane conversion at 8% based on 2-min runs followed by catalyst regeneration at 800°C with air for 30 min. By using sodium as the promoter and manganese acetate as the catalyst, methane conversions were increased to 15.2% with selectivities to 78.1% for C₂C₄ compounds. At low conversions (about 5%), selectivities of over 90% were reported by using sodium-pyrophosphate-promoted manganese oxide.

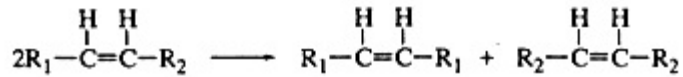
Work at Tokyo Institute of Technology [32]

Otsuka and coworkers screened 30 metal oxides in order to find the best catalyst. It was found that the oxides of rare earth elements have C₂-selectivities higher than 80%. Among the metal oxides tested, Sm₂O₃ was the most active and selective catalyst in the formation of C₂ hydrocarbons (selectivity 93%).

Methane is abundant in natural gas. In addition, it can be produced from syngas with high selectivity. Oxidative coupling of methane is in the early stage of development. This process may eventually become the new C₁ chemistry of the future.

Olefin Disproportionation [28]

The disproportionation (metathesis) reaction provides the basis for petrochemical processes which can interconvert commodity olefins, e.g., propylene, to more valuable ethylene and butylene. Research in the early 1960s by Banke and Bailey led to the general reaction for such monoolefins:

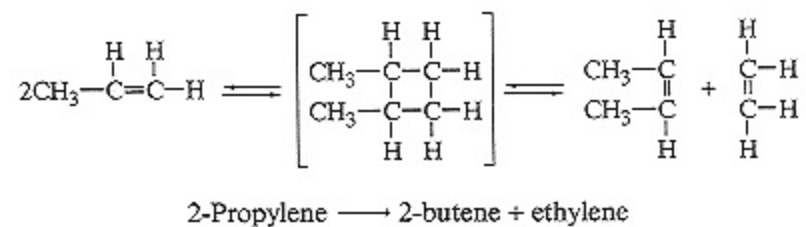


They found that olefins can be readily interconverted via a redistribution of structural configuration which, in effect, permits a controlled shuffling of molecular weights and double-bond placement. This reaction is called disproportionation.

The catalysts for the disproportionation reaction contain transition metals, preferably Mo, W, or Re, and are either heterogeneous or homogeneous. Heterogeneous catalysts are generally oxides deposited on a high surface area support, e.g., silicon or aluminum oxides. Homogeneous catalysts are derived from a transition metal halide used either alone or complexed with Lewis bases (e.g., triphenylphosphine) and a nontransition compound (e.g., ethyl aluminum dichloride).

Ethylene from Propylene [28]

Propylene can disproportionate, reacting with itself to yield ethylene and 2-butene.



Temperature 700850°F

Pressure 100 lb/in.2gauge

WHSV 40

Conversion 38.8%

Integration of a pyrolysis unit with a propylene disproportional unit is shown in Fig. 34.

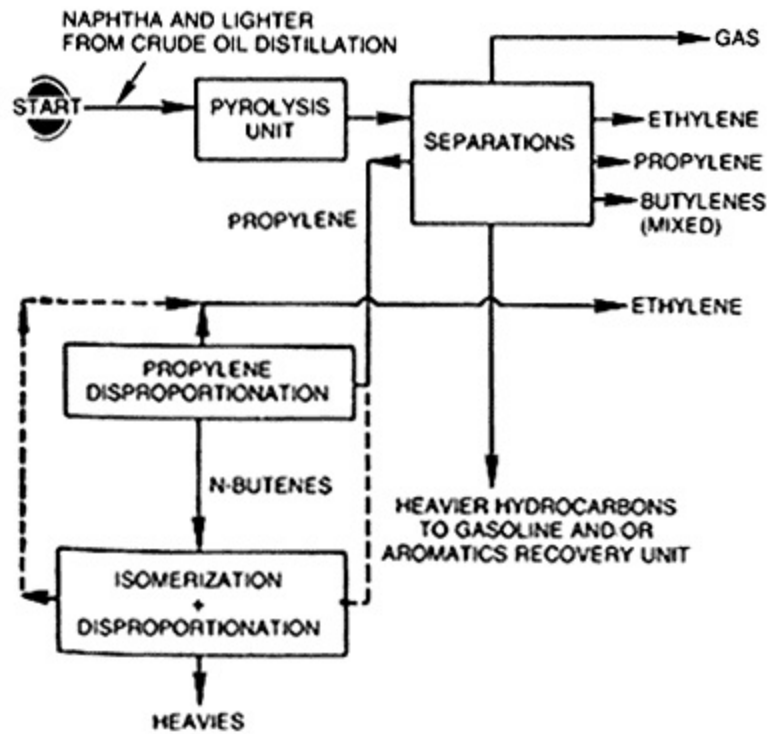


Fig. 34.

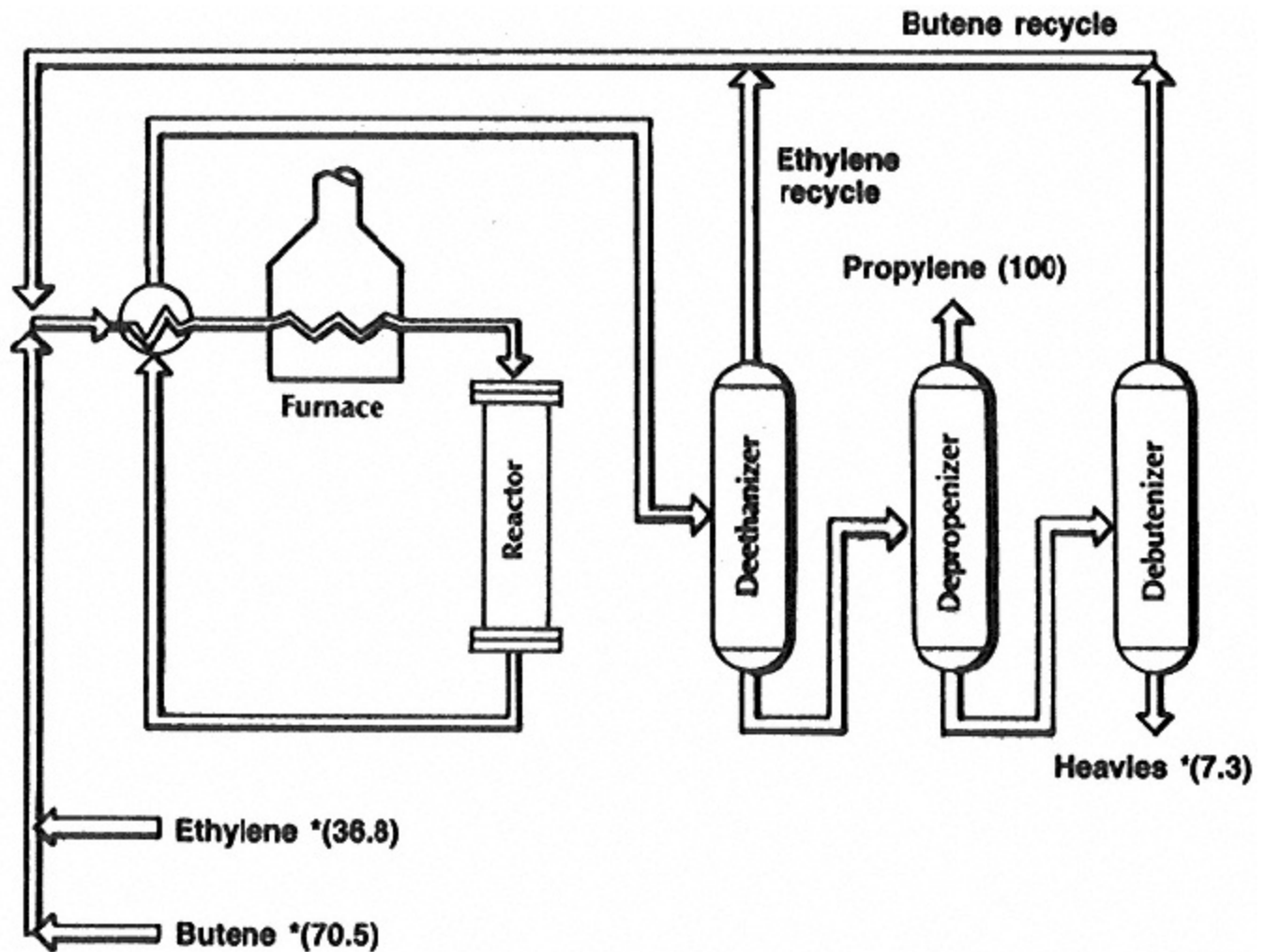
Additional ethylene production from naphtha steam cracker by addition of disproportionation unit.

Propylene from Ethylene and Butene [20]

The reaction to produce propylene is driven in the other direction. The process is shown in Fig. 35. An ethylene recycle stream is used to maintain the ethylene concentration in the reactor at several times the stoichiometric amount. By expanding this version to include an ethylene dimerization unit, butene can be obtained from ethylene without a separate source of 2-butene. In the ethylene dimerization step, ethylene and a homogeneous dimerization catalyst in a hydrocarbon solvent are fed to a loop reactor.

Catalytic Pyrolysis [29, 30]

Catalytic pyrolysis of hydrocarbons to produce olefins has the advantage of increasing selectivity, lowering reaction temperature, and increasing flexibility. Basic research on catalytic pyrolysis for the production of olefins has been conducted. Central to the study are the development of suitable catalysts, the mechanism of reactions, and the interaction between substrates and catalyst.



* Rates in percent of propylene product volume

Fig. 35.
Propylene from ethylene and butene.
Source: Phillips Petroleum Co.

The high yields of ethylene (between 30 and 40%) brought about by different catalysts at temperatures between 700 and 750°C appear to justify the intensive research work in this direction. Unresolved problems are the stability of catalysts and the regeneration required due to coke deposits.

Conventional pyrolysis has an ethylene/propylene ratio of 2:1; in catalytic pyrolysis this ratio is usually 1:1. The catalysts used for catalytic cracking are metal oxides of iron, chromium, cobalt, molybdenum, vanadium, and nickel.

The latest work by Phillips indicates that, compared with straight thermal cracking, both manganese and iron on magnesium oxide give a much higher conversion and selectivity to ethylene and ethane of such light hydrocarbons as n-butane, isobutane, and propane. Catalyst life was improved by mixing steam with the hydrocarbons feed and adding 2.7% calcium to the catalyst. The researchers believe the reason is that catalytic cracking produces both methyl and ethyl radicals, while thermal cracking produces only methyl radicals. With n-butane and propane feeds, the products from catalytic cracking include

large amounts of ethylene and ethane. With isobutane feed, propylene was the major product. The performances of various catalysts for different feedstocks are shown in Table 22.

TABLE 22

n-Butane Cracking (Temperature = 725°C, Steam/Hydrocarbons = 1)

Selectivity (%)

Catalyst	Conversion %	Ethylene	Ethane	Propylene	Methane
Fused silica	35	23	9	41	19
Mn-MgO	65	43	22	21	10
Fe-MgO	68	38	17	22	15

Propane Cracking (Temperature = 700°C)

Selectivity (%)

Catalyst	Conversion (%)	Ethylene	Ethane	Propylene	Butene	Methane
Fused silica	38	36	3	40	2	19
Mn-MgO	61	46	3	21	0	28

Isobutane Cracking

Selectivity (%)

Catalyst	Conversion (%)	Ethylene	Ethane	Propylene	Butene	Methane
Fused silica	32	3	1	31	50	14
Mn-MgO	59	3	1	47	23	23

aThermal cracking pressure = 1 atm.

Two patented catalytic processes claim high yields of ethylene by using naphtha or gas oil as the feedstock [30]: THR (by Tomita and Kitagawa) process and Fluor-Haldor Topsoe process. The catalysts for both processes are claimed to resist coke laydown.

Conclusions

During the past three decades, an impressive list of unconventional olefins processes has been developed. Each process has some of the following advantages:

Cheap raw materials

High yields and selectivities

Flexibilities in product distribution

Low energy consumption

Between 1981 and 1985 the petrochemical industry was in a difficult stage. Very few new steam crackers were built due to overcapacity, depressed product prices, uncertain oil prices, and competition among producers. The petrochemical industry has recovered since 1986. Many new ethylene plants are now planned. However, due to the cost of feedstock, all plants are based on conventional technology. In the late 1990s oil prices will rise, and some unconventional processes may become part of olefin production facilities.

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Oxidation of Aromatics

Ernest O. Ohsol

The principal products of aromatics oxidation are dibasic acids—the three phthalic acids (from naphthalene or xylene), and maleic acid or anhydride from benzene. Also, toluene can be oxidized to the monobasic acid, benzoic acid, as well as to the intermediate product, benzaldehyde.

Phenol is an oxidation product of benzene but is usually not made by direct oxidation, and is discussed separately. The same applies to the naphthols derived from naphthalene.

The principal problem in oxidation of aromatics with oxygen or air is that aromatics, being stable compounds, require relatively high reaction temperatures. However, once reaction has started, the intermediate products are much less stable and the reaction then tends to go toward complete oxidation to CO_2 and water. This is further exacerbated by the high heat of reaction which tends to drive temperatures out of control.

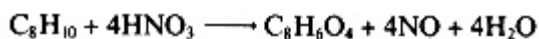
The problems have been solved in several ways:

1. By using catalysts which lower the reaction temperature and concurrently improve the selectivity of the reaction to the desired products.
2. By operating under high dilution, thus providing a heat sink and preventing temperature runaways.
3. By using very efficient heat-transfer systems in the reactor to control reaction temperature. This measure avoids the costly separation and recovery process entailed by Strategy 2.

Direct oxidation of aromatics is carried out commercially by both vapor-phase and liquid-phase processes. The liquid-phase processes are practiced at somewhat lower temperatures and therefore require somewhat more sophisticated catalyst systems.

Oxidation of p-Xylene to Terephthalic Acid

The largest quantity dibasic organic acid produced is terephthalic acid from p-xylene owing to its major use in polyester textile fibers. Originally, the acid was produced by liquid-phase oxidation of p-xylene with dilute nitric acid:

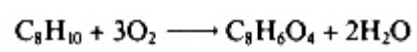


The nitrogen oxide was absorbed and recovered as nitric acid for re-use. There were a number of by-products, so the product acid was purified by esterification with methanol to dimethyl terephthalate, a liquid which was purified by distillation at reduced pressure. For making fiber, the purified dimethyl terephthalate was reacted directly at high temperature with pure ethylene glycol, methanol being vaporized from the polymerization reactor (thin film evaporators). The methanol could be purified and recycled. The polymer, polyethylene terephthalate, was stabilized, extruded, drawn, and cooled as a fine fiber. ICI's Terylene was the first (1949) of this genre, followed soon by DuPont's Dacron (1953).

Later, the size of the nitric acid oxidation system was reduced by using air oxidation in the first stage (liquid phase, catalyzed) for conversion to p-toluic acid, followed by nitric acid oxidation to terephthalic acid.

In the later 1950s Amoco and Scientific Design developed the liquid-phase oxidation technology now used (in various versions). When using pure p-xylene as the starting material, this process can produce a 99% pure terephthalic acid. This material can be hydrogenated to remove certain impurities, such as 4-formyl benzoic acid, and recrystallized to give a polymer-grade terephthalic acid. Figure 1 shows the basic steps in the oxidation process.

The solvent used is generally acetic acid, and the catalyst may be cobalt or cobalt with manganese, with bromide as the anion. The reaction produces water,



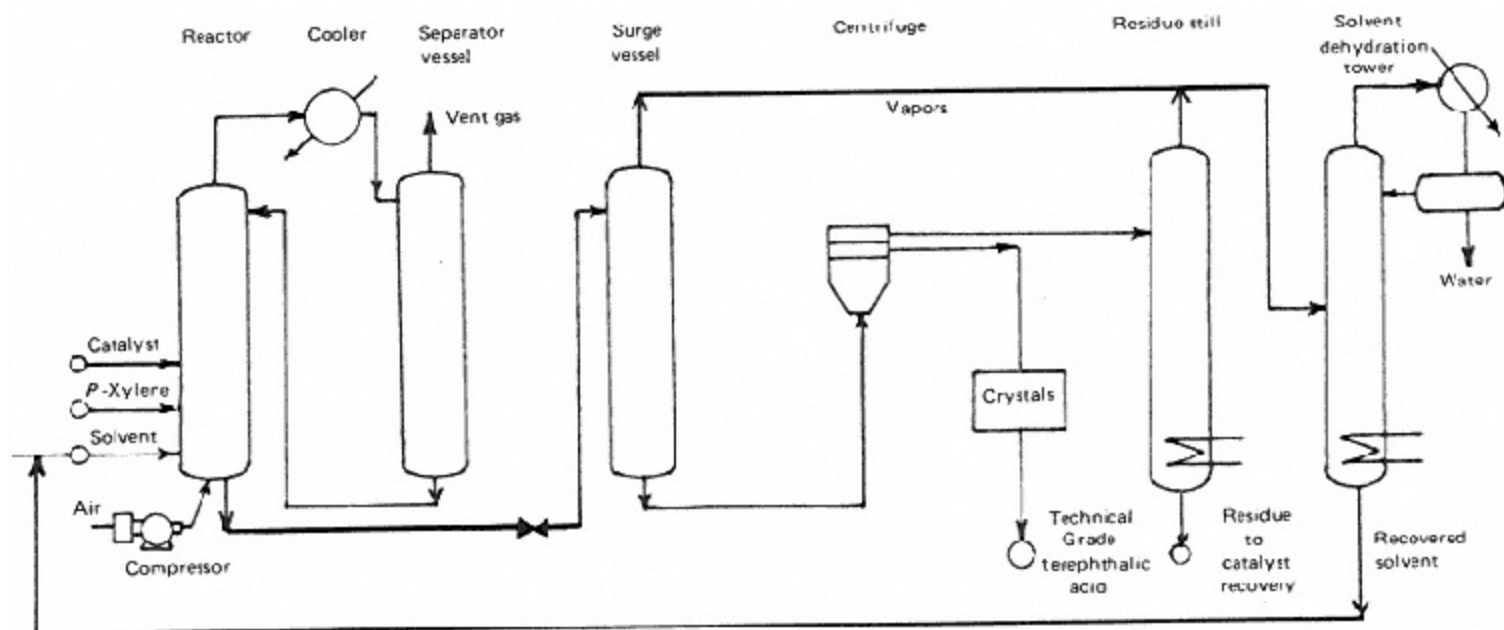


Fig. 1.
Liquid-phase p-xylene oxidation.

which insures that the system will be highly corrosive, requiring expensive alloy and/or glass-lined equipment. The reaction conditions are 175 to 230°C and 220 to 435 lb/in.² gauge (1500 to 3000 kPa). The reaction is strongly exothermic, giving off about 1300 kJ/g-mol, or approximately 5250 Btu/lb of xylene oxidized. The side reaction of complete oxidation liberates about three times this amount of energy, so it is apparent that close temperature control and efficient heat removal is necessary to prevent a runaway reaction. This is accomplished by circulating a considerable amount of acetic acid solvent, venting off vapors from the separator vessel.

The pressure is lower in the surge vessel, causing more vaporization and a temperature drop at which the bulk of the product terephthalic acid separates out and can be recovered as the solid in the centrifuge. After washing with fresh solution, technical-grade material is recovered.

The still residue is processed for catalyst recovery, and the overhead mother liquor, after dehydration, can be recycled to the reactor.

Polymer-grade terephthalic acid must be refined to better than 99.98% purity. This is usually accomplished by dissolving the acid in hot water, and pressurizing and hydrogenating the solution to convert difficulty soluble impurities like 4-formyl benzoic acid to more soluble products. The solution is then cooled and allowed to crystallize. The pure terephthalic acid is centrifuged out, washed, dried, and pulverized or granulated.

Other processes involve co-oxidation of acetaldehyde or paraldehyde with the xylene in a pressure liquid-phase reaction with air. Heat and water are removed by refluxing xylene and/or acetic acid.

Some producers still use methanol in the process, and the product is dimethyl terephthalate.

Some idea of the problems encountered in making and purifying terephthalic acid may be gleaned from the accompanying Table 1 showing its properties. It can be seen that not much product will be lost in a recrystallization from hot water under pressure.

o-Phthalic Acid and Anhydride

While o-phthalic acid can be made from o-xylene by liquid-phase oxidation in the same way as terephthalic acid from p-xylene, it is far easier to oxidize o-xylene directly to phthalic anhydride, $C_8H_4O_3$, a compound with a somewhat higher degree of stability than the free acids. Furthermore, the anhydride has a lower melting point and boiling point, making its recovery and purification an easier task. The free acid, if desired as the product, can be made by hydrating the anhydride.

Traditionally, o-phthalic acid and/or phthalic anhydride were formerly made from naphthalene because it was available in reasonably high purity from by-product coke ovens. In the last decades, however, there has been a growing shortage of coal tar

products and a growing capability of the petroleum industry to supply high purity o-xylene at reasonable cost. In the early days of naphthalene shortages when o-xylene was first substituted in vapor-phase oxidation, yields were low and new types of impurities were found in the product. More recently, superior catalysts and reaction control have led to

TABLE 1 Physical Constants of Terephthalic Acid and Dimethyl Terephthalate

	TPA	DMTPA			
Liquid:					
Freezing point, °C	427	140.6			
Boiling point, °C (at atmospheric pressure)		284			
Boiling point at 100 mmHg pressure		210			
Boiling point at 10 mmHg pressure		148			
Heat of vaporization, kJ/mol		57.3			
Solid					
Heat of sublimation, kJ/mol	142	88			
Sublimation point (at 1 atm)	404°C				
Vapor pressure of 100 mmHg at	353°C				
Vapor pressure of 10 mmHg at	303°C				
Density at 25°C, g/cm3	1.510	1.283			
Specific heat, J/kg·°C	1202	1400 (50°C)			
Solubility of TPA, g/100 g solvent:					
	Temperature, °C				
Solvent	25	120	160	200	240
Water	0.0019	0.08	0.38	1.7	9.0
Methanol	0.1		2.9		
Glacial acetic acid	0.035	0.3	0.75	1.8	4.5
Dimethylformamide	6.7				
Dimethylsulfoxide	20				
95% sulfuric acid	2				

yields from xylene matching those from naphthalene, and purity problems have almost disappeared.

The vapor-phase oxidation process is the preferred route to phthalic anhydride from either naphthalene or xylene. Figure 2 represents a typical production scheme. o-Xylene of 95% or higher purity is vaporized into a stream of air compressed to about 3 atm and fed into a molten-salt-cooled tubular reactor containing a modified supported vanadium pentoxide catalyst. The reactor temperature is held in the range of 385 to 455°C by regulating the flow of molten salt around the catalyst tubes. The heat of reaction is high, similar to that for p-xylene oxidation. The molten salt may be cooled in a separate waste-heat boiler. The xylene will be essentially completely converted to oxidation products; the yield of phthalic anhydride should be close to 85 mol% based on the pure o-xylene content in the feed.

The product gases pass from the reactor through a waste-heat boiler which generates steam. The gases, containing about 1 mol% phthalic anhydride, pass into a set of "switch condensers" in which the temperature is gradually lowered by cooling coils, causing the phthalic anhydride to condense first as a liquid and then as a solid on the coil surfaces. When the pressure drop through the condenser indicates it is nearly full, flow is switched to an alternate condenser and the first condenser is heated, rather than cooled, by using steam or hot oil in the coils. The phthalic anhydride melts and runs out into a receiver tank. The crude anhydride is then heated for a few hours in a

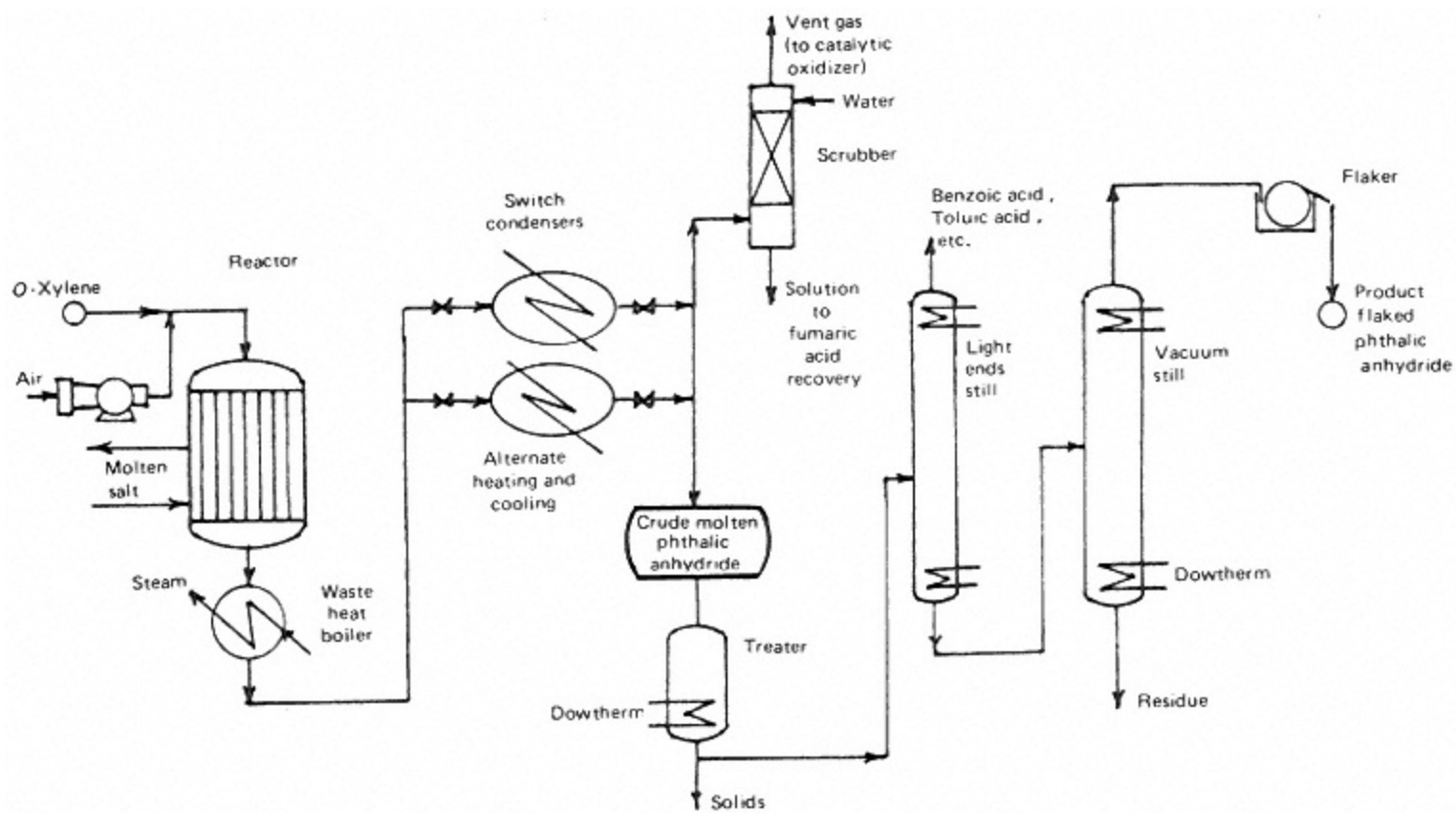


Fig. 2.
Vapor-phase o-xylene oxidation.

treater to polymerize quinones and other reactive impurities. It is then ready for final purification by distillation, first at atmospheric pressure to remove light ends and then under reduced pressure to leave a high boiling residue.

The uncondensed vapors leaving the switch condensers generally contain some maleic anhydride, and this can be remove in a water scrubber. It can easily be isomerized to fumaric acid, purified, and recovered as such. The tail gas will still contain some organic material which may be converted to CO₂ and water in a catalytic combustor.

Table 2 lists the physical properties of phthalic acid and phthalic anhydride. Phthalic acid decomposes to the anhydride at its melting point. When phthalic anhydride is dissolved in water, it slowly hydrates to the acid.

When phthalic anhydride is made from naphthalene, substantially the same process is used, except that naphthalene is vaporized into air in slightly more elaborate equipment. The heat of reaction from naphthalene is slightly higher, but since the starting material is more stable, slightly higher reactor temperatures (400 to 485°C) can be used, which makes heat removal somewhat easier. Yields from naphthalene are generally slightly higher in terms of percent of theory (about 90%).

Fluid-bed reactors have been successfully used for oxidizing naphthalene and xylene, with somewhat better results in the case of naphthalene. In a fluid bed a somewhat slower catalyst is generally used, giving greater flexibility in residence time. A simpler and cheaper heat-transfer surface can be used, but special care must be taken in separating catalyst fines from the converted gases to avoid building up an active runaway reaction zone in the separation device.

Isophthalic Acid from m-Xylene

This reaction is conveniently carried out by the Amoco-Scientific Design process described under terephthalic acid. Originally the liquid-phase reaction was carried out on mixed m-p-xylene, on the theory that the product

TABLE 2 Physical Properties Related to o-Phthalic Acid

Property	Phthalic Acid	Phthalic Anhydride
Melting point, °C	211 (decomposes)	131
Boiling point, °C (atmospheric)		284.5
Boiling point at 75 mmHg (10 kPa)		197
Solubility in water at 25°C, g/100 g water	0.7	0.6
Solubility in water at 100°C	19.0	16.5
Heat of formation, kJ/mol at 25°C	-782	-460
Specific gravity at 4°C, g/cm ³	1.593	1.527
Heat of fusion at 131°C (kJ/mol)		22.93
Heat of vaporization, kJ/mol		65.3

acids could be separated more easily than m- and p-xylene. Over the years it has been found that the reverse is likely to be true, and a relatively pure m-xylene can be obtained for oxidation to isophthalic acid. The physical properties of the iso-isomer are very similar to those of the tere-isomer, except for the melting points (427 for terephthalic and 348 for isophthalic, both subliming). The tere-isomer is even more insoluble in water than the iso-isomer.

Maleic Anhydride from Benzene

Oxidation of benzene to maleic anhydride,



is quite similar to the oxidation of naphthalene to phthalic anhydride,



Note that on a molar basis the heat of reaction should be about the same since the amount of oxygen reacting is the same, and to the same types of bonds.

However, maleic anhydride is a little less stable than phthalic anhydride, and the yields to the desired product are somewhat lower, about 75 to 80 mol% with the best catalysts (vanadium pentoxide modified with cobalt or other oxides on silica or SiC). Most of the by-products are highly oxidized CO_2 , CO, oxalic acid, formic acid; thus the actual heat of reaction is considerably above theoretical.

In condensing the product in about 1 mol% concentration from the reacted gases, a somewhat lower temperature is necessary than for phthalic anhydride (higher vapor pressure), so more water is condensed along with the product. A dehydration step is therefore necessary. Figure 3 is a schematic of a typical maleic anhydride plant (Halcon Process) starting with benzene. Table 3 shows the key physical properties of maleic anhydride, maleic acid, and fumaric acid.

Maleic acid is readily formed by the hydration of maleic anhydride; however, most of it is converted further to its trans-isomer, fumaric acid. Fumaric acid is difficultly soluble in water and can therefore be easily purified by recrystallization after isomerizing and decolorizing (with activated carbon) the maleic acid solution. The isomerization is readily carried out by moderate heating in the presence of a catalyst such as thiourea. Fumaric acid is nontoxic and sometimes used in foods, whereas maleic acid is quite toxic. Maleic anhydride is usually sold as a liquid in heated containers or as flakes in cool environments.

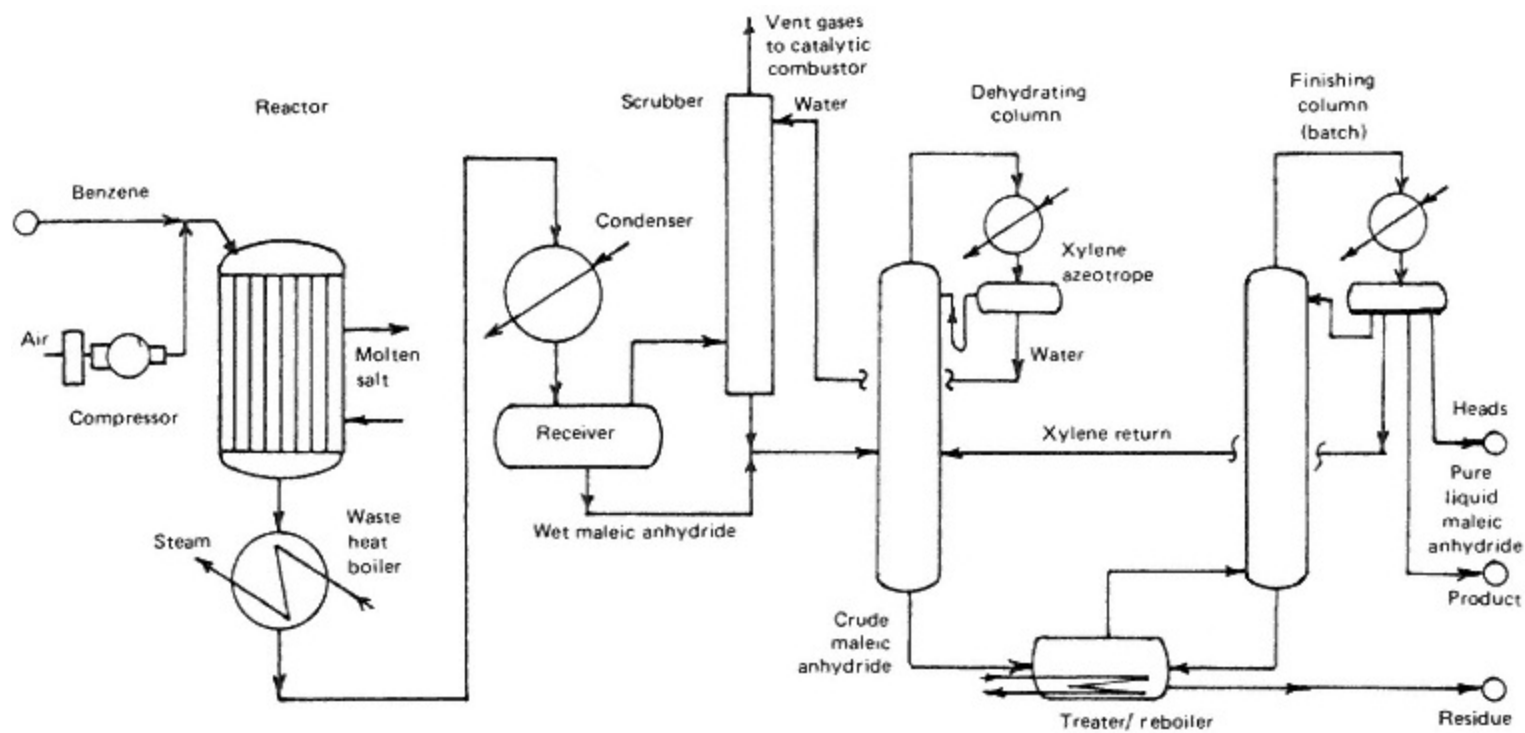


Fig. 3.
Benzene oxidation to maleic anhydride.

TABLE 3 Physical Properties Related to Maleic Anhydride

Property	Maleic Anhydride	Maleic Acid	Fumaric Acid
Melting point, °C	52.85	130.5	287
Boiling point, °C	202	Sublimes at 165°C and 0.23 kPa	
Specific gravity 20/20 (solid)	1.48	1.59	1.635
Specific gravity 70/70 (molten)	1.3		
Heat of formation, kJ/g-mol	-470.41	-790.57	-811.03
Heat of vaporization, kJ/mol	54.8		
Heat of fusion, kJ/mol	13.65		
Heat capacity (solid), kJ/mol	1.21		
Heat capacity (liquid)	1.67		
Solubility in water, g/100 g solution:			
Temperature, °C	Solubility		
25		44.1	0.70
40		52.9	1.05
60		59.8	2.34
97.5		79.7	
100			8.93

Other Aromatic Oxidations

Benzoic acid and/or benzaldehyde is commercially produced by the liquid-phase oxidation of toluene with air at relatively mild conditions, i.e., pressure in the range of 3 to 8 atm and temperature in the range of 130 to 160°C. The catalyst is 30 to 1000 ppm cobalt. Yields of about 90% of theory are obtained. Other processes using chlorine or decarboxylating phthalic acid can be used, but they are normally not competitive.

Other specialty benzene carboxylic acids are made in modest quantities from the corresponding polymethyl benzene; for example, trimellitic acid (1,2,4-benzene tricarboxylic acid) from 1,2,4-trimethyl benzene, and pyromellitic acid (1,2,4,5-benzene tetracarboxylic acid) from durene (1,2,4,5-tetramethyl benzene). Both of these products can form anhydrides (or even a dianhydride, in the case of the latter), making them more useful intermediates. They are generally produced by liquid-phase nitric acid oxidation.

Oxidation of Hydrocarbons

Charles C. Hobbs
and Michael B. Lakin

Introduction

The challenge of direct conversion of alkanes to commodity chemicals has existed since petroleum began to be recovered in significant quantities. Oxidations of these substrates have been studied for well over a century, but it was not until the 1930s that modern understanding of the processes began to develop. A number of reviews on the subject have been published [17], but much controversy remains about the relative importance or even the existence of proposed individual steps. However, for the purposes of this discussion, the simplified scheme presented below is adequate to develop an understanding of some key factors that influence process design and operation.

Both vapor-phase oxidations (VPO) and liquid-phase oxidations (LPO) of lower alkanes (propane, butane) have been operated commercially; however, the vapor-phase processes are largely of historical interest. The major products were acetaldehyde (subsequently converted to acetic acid), formaldehyde, methanol, and acetone. The last VPO process was shut down in 1972 as a result of various economic factors, particularly energy requirements for purification of complex product mixtures. Liquid-phase n-butane oxidation

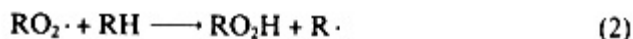
processes are still operated by Celanese at Pampa, Texas, and at Edmonton, Alberta, Canada. These plants produce about 700 million pounds per year of acetic acid (total United States production in 1984 was 2.8 billion pounds [8]) as well as significant quantities of methyl ethyl ketone and other coproducts.

Some other liquid-phase oxidations of commercial importance are p-xylene to terephthalic acid; cumene to phenol and acetone; isobutane to tert-butyl hydroperoxide (used to make propylene oxide) and tert-butyl alcohol; cyclohexane to cyclohexanol, cyclohexanone, adipic acid, etc. (nylon raw materials); ethylbenzene to styrene (intermediate hydroperoxide used to make propylene oxide); higher alkanes to fatty acids (mostly in Eastern Bloc countries); and aldehydes to acids (e.g., heptanal to heptanoic acid).

Oxidation Reaction Mechanisms

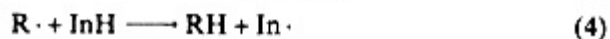
In both VPO and LPO processes, similar reaction mechanisms appear to be operative [9] although the relative importance of individual steps can be markedly different.

Hydrocarbon oxidations are essentially chain reactions which produce hydroperoxides as important intermediates or products. The propagation steps of a simple peroxide-producing chain can be represented as follows:



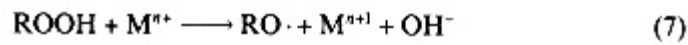
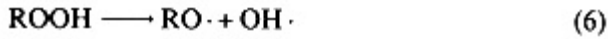
An important aspect of such reactions is that, by and large, the hydrocarbon substrate does not react with oxygen. Oxygen reacts almost exclusively with radicals bearing an unpaired electron on carbon to produce oxygenated radicals. These radicals then bring the hydrocarbon molecules into the sequence by hydrogen abstraction (e.g., Reaction 2). Reaction (1) is very rapid in comparison to Reaction (2) so that $[RO_2 \cdot]/[R \cdot]$ is usually very high unless the concentration of oxygen is quite low [7].

To sustain a chain reaction, a radical flux must be provided in the reactor. This requires not only a source of the initial radicals but also a continuing source of new radicals to replace those lost in chain termination reactions such as those shown below:



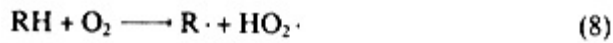
Chain terminations can occur in bimolecular reactions of radicals (usually peroxy radicals) in which the unpaired electrons of the reactants are paired in the products or in reactions between radicals and inhibitors. In the latter case an active radical can either abstract hydrogen from or add to an inhibitor to produce a radical which is too weak to continue the chain.

The continuing source of new radicals is usually the thermal or catalytic decomposition of hydroperoxide [10]:



where M^{n+} is a metal ion in the $n+$ oxidation state. In at least some cases, the higher valence state ion produced in Reaction (7) also has hydrogen abstraction capability.

We still have not addressed the question of the source of the original radicals required to start the reaction. The answer is still controversial, but one common proposal is



Other reactions have been proposed as well as the presence of traces of peroxides in the feed materials. Whatever the source, the reaction can be very slow during this phase, which is frequently referred to as the "induction period." Plug flow, adiabatic systems (e.g., many of the processes using vaporphase reactors) show imperceptible reaction over most of the flow path until the reaction suddenly accelerates vigorously (see . 1). Backmixed, nonadiabatic systems (e.g., most individual LPO stages) are usually heated to a temperature significantly above the normal reaction temperature during the start-up period to get the reaction started quickly. The presence of catalysts shortens the start-up phase by increasing the rate of peroxide decomposition.

Another important facet of chain reactions is the chain length. This is essentially the average number of moles of oxygen consumed by Reaction (1) for each new radical introduced into the system. If Reaction (2) is sufficiently

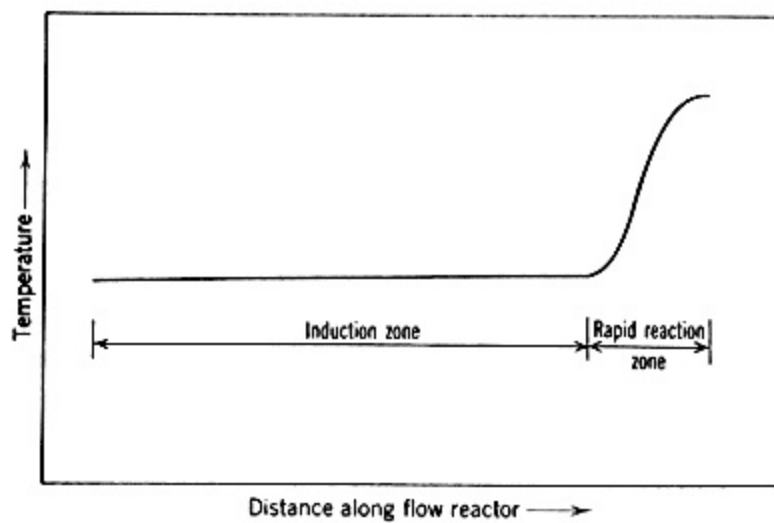
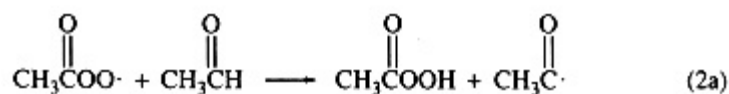
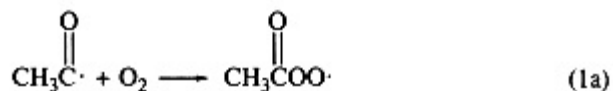
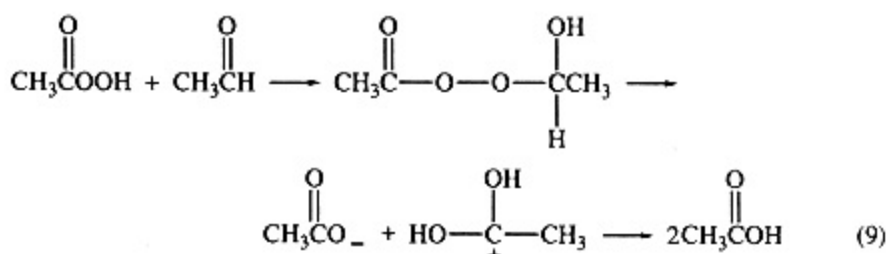


Fig. 1.
Temperature profile of propane VPO in a flow reactor.

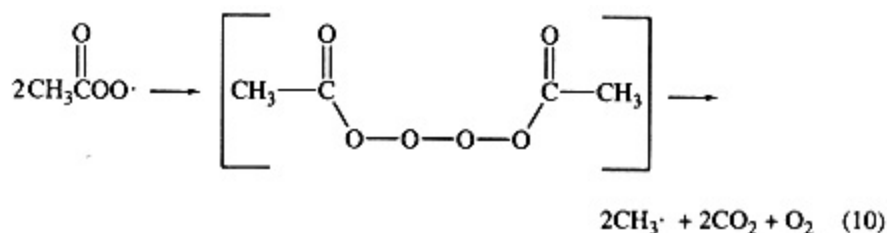
rapid in comparison to the termination reactions (Reaction 3, 4, and 5), the kinetic chain can be quite long (100 cycles or more). The oxidation of acetaldehyde is a good example:



In this case the intermediate hydroperoxide (peracetic acid) reacts with acetaldehyde to give a complex which decomposes to acetic acid [11]:



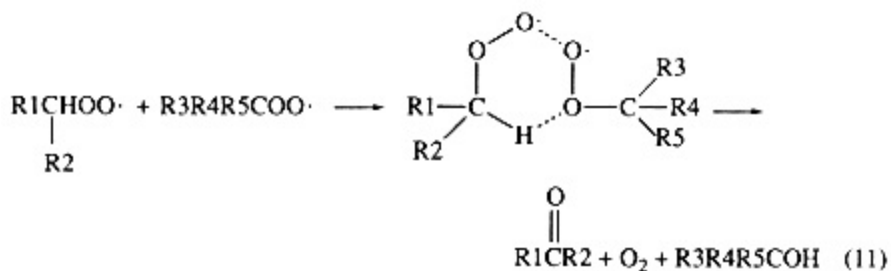
The analog of Reaction (3) is somewhat more complex in this case:



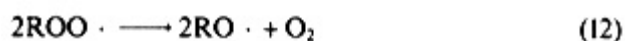
Since methyl radicals are produced, this is not the final termination step. The actual termination involves methylperoxy radicals made from the methyl radicals (see Reaction 11 below) [12]. The chains are long in this case because Reaction (2a) with acetylperoxy radicals is fast in comparison to Reaction (11) with methylperoxy radicals. This permits high efficiencies to acetic acid with minor losses to carbon dioxide and methyl derivatives (methanol, formic acid, etc.).

In most hydrocarbon oxidations, however, Reaction (2) is somewhat slower with respect to the termination reactions. At the high specific reaction rates achieved in many commercial processes, peroxy radical concentrations build up to high levels and the radicals have more opportunity to engage in second-order termination reactions. The chains, therefore, can be much shorter, in the 3 to 10 range, and in some cases even shorter [10]. As a consequence, chain termination reactions make a greater contribution to the products.

A major termination reaction involving at least one primary or secondary alkylperoxy radical is



Nonterminating reactions of alkylperoxy radicals also occur; alkoxy radicals are produced [13, 14]:



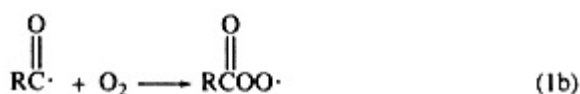
Bimolecular radical reactions of tertiary alkylperoxy radicals are largely restricted to Reaction (12); this reaction can occur to some extent with the less highly substituted alkoxy radicals as well [15].

It is by now obvious that the steps for the oxidation of a hydrocarbon are complex and subject to wide variations depending on various kinetic and structural factors. This complexity is compounded since any free radical chain oxidation is inevitably a cooxidation of the hydrocarbon and its products. Free radicals abstract hydrogens on the basis of random encounters under the restraint of reactivity factors. Therefore, any product lower than carbon dioxide in the oxidation state scale [16] is at some risk of further oxidation. Many products are the result of multistep sequences [17, 18].

The historical vapor-phase alkane oxidation reactions utilized propane and butane at moderate pressures (~ 125 lb/in.² gauge). The products were mostly alcohols, aldehydes, and ketones. From propane, for example, the major products were acetaldehyde, formaldehyde, methanol, and acetone. Very little acid was produced since the efficient oxidation of aldehydes was precluded by decomposition of intermediate acyl radicals:



This reaction also accounts for the predominance of CO in the carbon oxides produced in VPO. Reaction (13) competes very strongly with

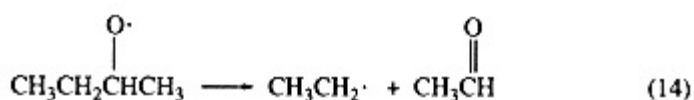


because of the high temperatures and low partial pressures of oxygen. At higher total pressures (e.g., 2000 lb/in.² gauge), Reaction (1b) can compete

more effectively (higher partial pressures of oxygen) and acids become significant products [7]. Because VPO lacks current commercial importance, the remainder of this discussion is devoted to LPO.

The LPO of n-butane produces mostly acetic acid with relatively lesser amounts of coproducts such as methyl ethyl ketone, formic acid, propionic acid, butyric acid, acetone, ethanol and methanol (and their esters), γ -butyrolactone, and some high boiling material (succinic acid, aldol products, etc.). Methyl ethyl ketone and sec-butyl alcohol appear to be produced mostly by Reaction (11). The sec-butyl alcohol is rapidly oxidized to methyl ethyl ketone.

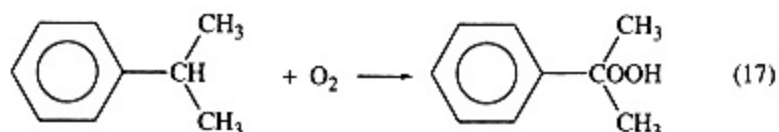
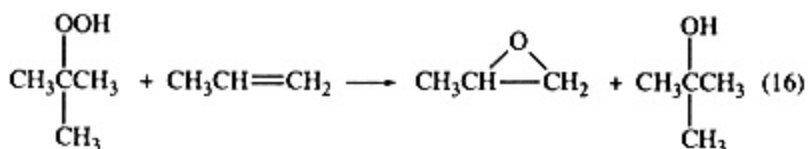
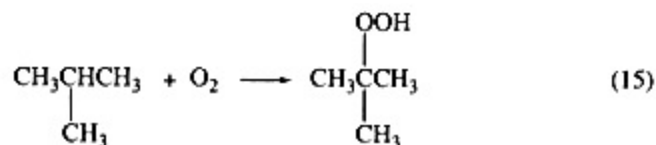
The most important reaction pathway, however, appears to be through sec-butoxy radicals (from Reactions 6, 7, and 12):

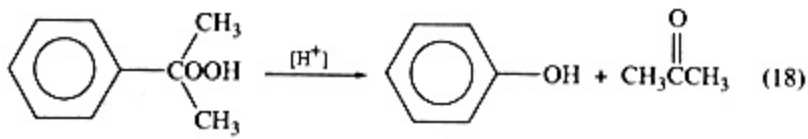


Reaction (14) is an example of a β -scission reaction. The ethyl radical is efficiently converted to ethanol which is then quickly oxidized to acetaldehyde. Acetaldehyde is rapidly converted to the major product, acetic acid. Acetic acid is rather resistant to further oxidation and most of it survives in the product [7].

The liquid-phase oxidations of higher alkanes are in many ways similar but with additional complexity. When oxidized, these molecules can undergo multiple intramolecular hydrogen abstractions which can lead to the production of shorter chain methyl ketones and difunctional intermediates [19].

In some oxidations the goal is to produce a hydroperoxide. This is most successful where the hydroperoxy group replaces a tertiary hydrogen, but is not limited to this case. Examples are the production of tert-butyl hydroperoxide from isobutane and cumyl hydroperoxide from cumene. The first product is used mostly to epoxidize propylene (Reactions 15 and 16) while the second is converted to phenol (Reactions 17 and 18).





These reactions are, in general, conducted under conditions to maximize the survival of the primary hydroperoxide. This means low temperatures and low rates (longer chain lengths) and, usually, the absence of metal ion catalysts. The aromatic oxidations are frequently done in a two-phase system in which an alkaline aqueous phase extracts acidic by-products which promote decomposition of the peroxide.

Saturated cyclic hydrocarbons generally produce monofunctional cyclic alcohols and ketones and open-chain difunctional products (especially acids and hydroxy acids). The oxidation of cyclohexane, for example, gives cyclohexanone and cyclohexanol as well as adipic acid, hydroxycaproic acid, and others. The cyclohexanone and cyclohexanol can be further oxidized to adipic acid by nitric acid. The one-step oxidation of cyclohexane to adipic acid using air as the oxidizing agent has also been developed. Several variations on this chemistry account for much of the raw materials used for nylon [7].

Cyclohexane oxidation is generally conducted at low conversion and frequently in staged reactors to maximize efficiencies to the intermediates cyclohexanone and cyclohexanol.

Oxidation Reactor Design

Many factors demand consideration in the design and scale-up of LPO and other gas-liquid reactors. These factors concern the system's physical and chemical kinetic parameters, as well as its fluid dynamic properties. In addition to the chemistry already described, these encompass gas bubble size, rousing factor (ratio of gassed liquid volume to ungassed liquid volume), and sparger character; system physical properties; reactor bulk flow and mixing dynamics; and heat and mass transfer behavior. Furthermore, one must choose a commercial reactor type and operation mode which will function in the most economical manner.

Fluid Dynamics

The nature of the fluid dynamic regime created in the LPO reactor, as reflected in the characteristic bubble size and shape observed, is controlled by several design elements:

Equipment variablesparger and column geometry

Physical system propertiesgas and liquid density, viscosity, surface tension, diffusivity, and dispersion character

Operating variablesflow rates, temperature, and pressure

Because these factors exert a strong influence on the dynamic behavior of the system, they also play an important role in determining the process result. The understanding of the effects of most of these design parameters is still largely empirical; however, there are a few useful engineering guidelines.

While sparger designs abound and have been widely studied, the simple perforated-pipe, multi-orifice gas sparger remains a preferred design for practical reasons; these especially include ease of design and operation. For orifice diameters less than about 6 mm and orifice Reynolds numbers exceeding 30,000, the Sauter (volume-to-surface) mean bubble diameter obtained is in the range of 0.5 to 6 mm [2023]. This bubble size remains relatively constant in the homogeneous or bubbling flow (noncoalescence) regime which is generally observed at superficial gas velocities less than ~ 6 cm/s [2023]. Adequate bubble size estimates can be obtained from a number of literature correlations [2426]. However, because some of these have been correlated to superficial gas velocity, these estimated values must be corrected for volatile stripping effects which tend to increase the initial bubble size. For all sparger designs, care must be exercised to design for the gas distribution and mixing behavior consistent with the desired process result.

An important parameter in describing LPO with a gaseous oxidant is the rousing factor. This factor is defined as the ratio of the gassed (roused) liquid volume to the ungassed or true liquid volume. In terms of the characteristic bubble velocities it can be shown that

$$RF = U_b / (U_b - U_s) \quad (19)$$

Where
 RF = rousing factor = $\frac{(\text{liquid volume} + \text{volume of bubbles})}{\text{liquid volume}}$

U_s = superficial gas velocity, volume of gas fed per unit
 time per unit cross-sectional area

U_b = bubble rise velocity, distance per unit time

The rousing factor is obviously not a unique function of superficial gas velocity but is also dependent on all the system parameters that determine bubble rise velocity (physical properties, sparger type, geometry, etc.). Bubble rise velocities tend to be relatively constant for a given system over fairly broad ranges of variable values, but marked departures can occur under conditions that are highly individual to each system. Presently, there is no satisfactory correlation for predicting rousing; laboratory and/or pilot-plant measurements are necessary and recommended.

Flow patterns and mixing in the LPO reactors are complex functions of a number of factors because the geometry of such bubble columns is relatively unstructured. Thus, gas rates and distribution, sparger design, and liquid recycle rates and distribution, as well as internal reactor geometry, exert an influence on the system's fluid dynamic behavior.

While liquid-phase recycles can promote a well-mixed liquid phase, the agitation provided by the gas bubbling is usually even more effective in this regard. The LPO reactor mixing characterization can be obtained either by estimating the Peclet number (ratio of mass transport by bulk flow to that by dispersion) of each

fluid phase, or by performing radioisotope tracer tests of each fluid phase and analyzing the resultant tracer curves. For commercial LPO reactors with low aspect (i.e., height to diameter) ratios, a well-mixed liquid phase is ensured; the gas phase usually exhibits intermediate (between well-mixed and plug flow) mixing behavior. For tall cylindrical reactors (i.e., large aspect ratio), the liquid phase will demonstrate well-mixed to intermediate mixing behavior while the gas phase will show intermediate to plug-flow mixing. Designing for the desired mixing condition will depend on balancing the needs for the system's kinetic and mass transfer characteristics (see mass transfer discussion) as well as economic considerations.

Heat Removal

Hydrocarbon oxidations are very exothermic, so reactor system designs must include high capacity heat removal capability. It is intriguing to note that the rate of heat release is, in general, almost a direct linear function of the rate of oxygen consumption; i.e., within limits, the heat released per unit of oxygen consumed is relatively independent of the substrate being oxidized or the product distribution. The "heating" value of oxygen, in this sense, is about 108 ± 5 kcal/g-mol O_2 consumed for many feeds and products. Some components, especially aldehydes and carbon monoxide, cause deviations outside this range.

The two most common methods for removal of heat from an oxidation reactor are contact of the reactor liquid with a heat-exchange surface and vaporization of volatile components. Heat exchange with the reactor liquid can be either internal or external to the reactor. External cooling usually requires a rapid circulation rate; recycle/take-off ratios are typically $>100:1$. Fouling of heat exchanger surfaces is a significant problem with this type of system.

Heat removal by vaporization of liquid components is possible when sufficient inert gas (CO_2 , N_2 , etc.) and sufficiently volatile liquid material are present. This approach is applicable, for example, to n-butane LPO using air. A limiting concern in such a case is that the vapor load will reduce the concentration of oxygen in the rising bubbles too much; this can lead to oxygen starvation or reaction cessation if allowed to proceed too far. Reaction cessation can be particularly hazardous since it usually leads to combustible mixture compositions in the vapor space or at some point during condensation of the overhead vapors.

Oxygen Mass Transfer

The mass transfer of oxygen from the vapor to the liquid phase is a critical part of any liquid-phase oxidation using air or oxygen as the oxidizing agent. The characteristics of mass transfer to a large extent dictate reactor design and will be examined in some detail. The influence of mass transfer on such design features as total reactor volume and aspect ratio (height vs diameter) will be discussed. Although mass transfer is a very complex phenomenon,

some simplifying assumptions can lead to an easy and at least semiquantitative understanding of the effects involved.

A simplified schematic representation of an idealized liquid-phase oxidation system with a simple sparger is shown in Fig. 2. We will consider here the use of air as the oxidant. Let us assume: (1) that the emerging bubbles are formed instantly and immediately become saturated with the vapor of the reactor solvent, (2) that the bubbles rise independently, and (3) that the bubble rise velocity is constant. The first assumption ignores the small distance above the sparger over which the bubbles are forming and reaching steady state. The second assumption is a reasonable approximation as long as the superficial gas velocity (see above) is not too high. The third assumption is less satisfactory, but is still acceptable as a crude approximation because: (1) only about 20% of the gas in the bubble is consumable (O_2); (2) the consumed oxygen is partially replaced by gaseous products (CO and CO_2); (3) there is some offsetting effect as a result of reduced hydrostatic head as the bubble rises (more important at low pressures); and (4) in the turbulent region where most reactors operate, bubble rise velocity will vary approximately as the

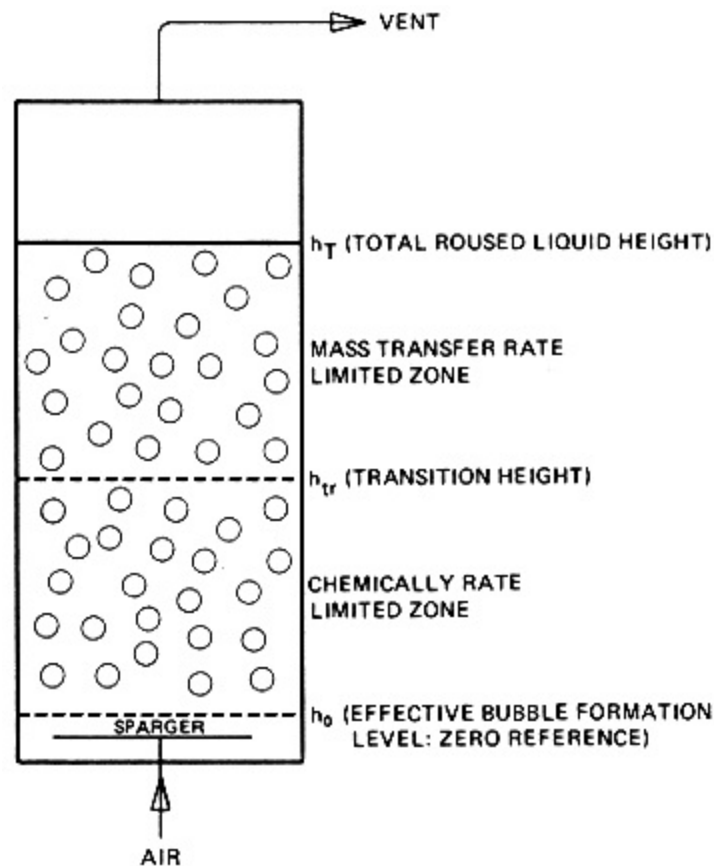


Fig. 2.
Idealized liquid-phase oxidation reactor.

square root of bubble diameter [27] and is, therefore, relatively insensitive to bubble size.

There will, in general, be two characteristic zones (plus a transition region) present in LPO. In the vicinity of the sparger the reaction will be chemically rate limited provided the initial partial pressure of oxygen in the bubble is sufficient to supply all the oxygen that can be consumed by Reaction (1). Over some range the rate will be independent of oxygen partial pressure in the bubble since, given sufficient oxygen in solution, the rate of Reaction (1) is limited by the rate of Reaction (2), which is independent of oxygen concentration. The rate in the chemically rate limited zone (CRLZ) is therefore zero order with respect to oxygen [28].

As the concentration of oxygen in the bubble falls, a point is eventually reached where the oxygen mass transfer mechanism is no longer able to supply oxygen at the maximum rate (the limiting kinetic rate, LKR) at which it can be consumed by Reaction (1). As the oxygen concentration in solution continues to fall, Reaction (1) becomes rate controlling. The overall rate is then limited by the rate at which oxygen can be transferred from the vapor phase into the liquid phase. This zone is called the mass transfer rate limited zone (MTRLZ). There is, of course, a transition zone, but this can generally be treated as negligible.

If we assume that the partial pressure of oxygen in equilibrium with the concentration of oxygen in the liquid in the MTRLZ is negligible in comparison to the partial pressure of oxygen in the bubble, then the first-order model described above will yield

$$P_{O_2}^{h_2}/P_{O_2}^{h_1} = e^{-(h_2-h_1)/h_{\tau}} \quad (20)$$

where $P_{O_2}^{h_i}$ = partial pressure of O₂ in an average gas bubble at h_i

h_i = height above sparger at level i (cm)

h_{τ} = transfer height (cm) the distance over which the 11/e fraction (~63%) of the oxygen in an average bubble is transferred to the liquid in the MTRLZ; this is a function of a number of system variables including the mass transfer coefficient, superficial gas velocity, bubble size, rousing, and gas solubility characteristics

In contrast, in the CRLZ, the "degree of reaction" (i.e., the conversion of oxygen) for any column height is directly proportional to the column height:

$$P_{O_2}^{h_2}/P_{O_2}^{h_1} = 1 - FCR \times (h_2 - h_1) \quad (21)$$

where FCR = "fractional chemical rate" (cm⁻¹).

The FCR is defined as the fraction of the input oxygen which is consumed per unit height of roused liquid column when the rate is not limited by the oxygen supply. It can be calculated from the limiting kinetic rate (see below) as follows:

$$\text{FCR} = \frac{\text{LKR} \times \text{CSA}}{\text{OFR} \times \text{RF}} \quad (22)$$

where $LKR = \frac{\text{"limiting kinetic rate," maximum mmol O}_2 \text{ consumed/s/cm}^3 \text{ true liquid volume at a specific temperature (see Eq. 25)}}$

CSA= cross-sectional area of reactor (cm²)

OFR= oxidant feed rate (mmol O₂/s)

If we assume the transition zone is negligible, the relationship of oxygen partial pressure in the vent to oxygen partial pressure in the feed for an ideal two-zone reactor can be shown to be

$$\frac{P_{O_2}^V}{P_{O_2}^F} = \frac{FCR \times h_t}{e^{(h_t - h_0 - l)/FCR + k_L h_t}} \quad (23)$$

where $P_{O_2}^V$ = partial pressure of O₂ in the vent gas (atm)

$P_{O_2}^F$ = partial pressure of O₂ in the feed gas (atm)

h_T= total roused liquid column height (cm)

h₀= zero reference level (see Figs. 2 and 3)

A plot of the partial pressure of oxygen in an average bubble in a two-zone

TABLE 1 Data for MEK Oxidationa

Observation No.	Temperature (°C)	$P_{O_2}^V / P_{O_2}^{Fb}$	Rousing factor ^b	Observed OCR _b × 10 ³ mmol O ₂ /s/cm ³	Calculated LKR _b × 10 ³ mmol/s/cm ³
1	130	0.0553	1.1952	1.1095	2.9401
2	127.3	0.0579	1.1878	1.0996	2.3899
3	125	0.0684	1.1815	1.0816	1.9988
4	122.3	0.0805	1.1749	1.0616	1.6162
5	120	0.0989	1.1697	1.0358	1.3456
6	117.5	0.1421	1.1647	0.9819	1.0998
7	115	0.2368	1.1600	0.8700	0.8966
8	112.5	0.3816	1.1557	0.7023	0.7290
9	110	0.5158	1.1518	0.5840	0.5912
10	107.5	0.5684	1.1482	0.4870	0.4780
11	105	0.6211	1.1448	0.4262	0.3855
12	102.5	0.7263	1.1417	0.3071	0.3100
13	100	0.7895	1.1388	0.2356	0.2485
14	97.5	0.8316	1.1361	0.1880	0.1987
15	95	0.8737	1.1336	0.1407	0.1583
16	92.5	0.8868	1.1312	0.1258	0.1258
d	131.87		1.2000		3.3883
d	114.28		1.1588		0.8447

aData for Run 3 of Fig. 4 and 5 (see Ref. 28): OFR $b = 0.8347 \text{ mmol O}_2/\text{s}/\text{cm}^3$; $\text{CSAb} = 20.27 \text{ cm}^2$; effective liquid column height =41.91 cm.
bSee Symbols.
c τ calculation fails because little MTRLZ b remains;
 $h\tau \text{ avg} = 14.59 \pm 0.20$
dCalculated limiting values.

(Table continued on next page)

reactor as a function of height above the sparger is shown in Fig. 3 (data taken from Observation 4, Table 1). The following points are worth noting:

1. The partial pressure of oxygen in the bubble drops linearly with h until the transition height (h_{tr}) is reached
2. $P_{O_2}^h/P_{O_2}^F$ follows a first-order decay curve above h_{tr}
3. A tangent from the curve at h_{tr} intercepts the x axis h_τ units above h_{tr}
4. $h_{tr} + h_\tau = 1/FCR$

As an example, a plot of the concentration of oxygen in the vent as a function of temperature for a real reactor in which methyl ethyl ketone is being oxidized with air at several different air rates (cobalt catalyst) is shown in Fig. 4 [28]. Such a reaction is started by heating to a temperature at the high end of the scale. The oxygen concentration in the vent falls to a very low value after a short induction period. As the temperature is lowered, the oxygen in the vent rises almost imperceptibly at first. Eventually, a point is reached where the oxygen in the vent rises very rapidly. The temperature at which this

(Table continued from previous page)

Observation No.	FCR ^b (cm-1)	h_τ^b (cm)	h_{tr}^b (cm)	Calculated $P_{O_2}^V/P_{O_2}^F$ at $h_\tau = 14.59$ cm	Calculated h_{tr} at $h_\tau =$ 14.59 cm	% V_{CRLZ}^b	% R_{CRLZ}^b
1	0.05973	14.42	2.32	0.0571	2.16	5.15	13.68
2	0.04886	14.35	6.12	0.0603	5.88	14.07	30.56
3	0.04108	14.82	9.53	0.0661	9.76	23.28	42.91
4	0.03340	14.75	15.19	0.0789	15.35	36.62	55.66
5	0.02793	14.62	21.18	0.0986	21.21	50.62	65.73
6	0.02293	14.59	29.02	0.1383	29.02	69.26	77.23
7	0.01877	c		0.2196	38.69	92.32	93.05
8	0.01532			0.3581	41.91	100	100
9	0.01246			0.4777	"	"	"
10	0.01011		0.5763	"	"	"	"
11	0.00818		0.6573	"	"	"	"
12	0.00659		0.7237	"	"	"	"
13	0.00599		0.7779	"	"	"	"
14	0.00425		0.8221	"	"	"	"
15	0.00339		0.8579	"	"	"	"
16	0.00270		0.8869	"	"	"	"
d	0.06856		0.0566	0	0	0	0
d	0.01770		0.2582	41.91	100	100	100

aData for Run 3 of Fig. 4 and 5 (see Ref. 28): OFR $b = 0.8347$ mmol O₂/s/cm³; CSAb = 20.27 cm²; effective liquid column height = 41.91 cm.

bSee Symbols.

ch τ calculation fails because little MTRLZ b remains;

h_τ avg = 14.59 ± 0.20

dCalculated limiting values.

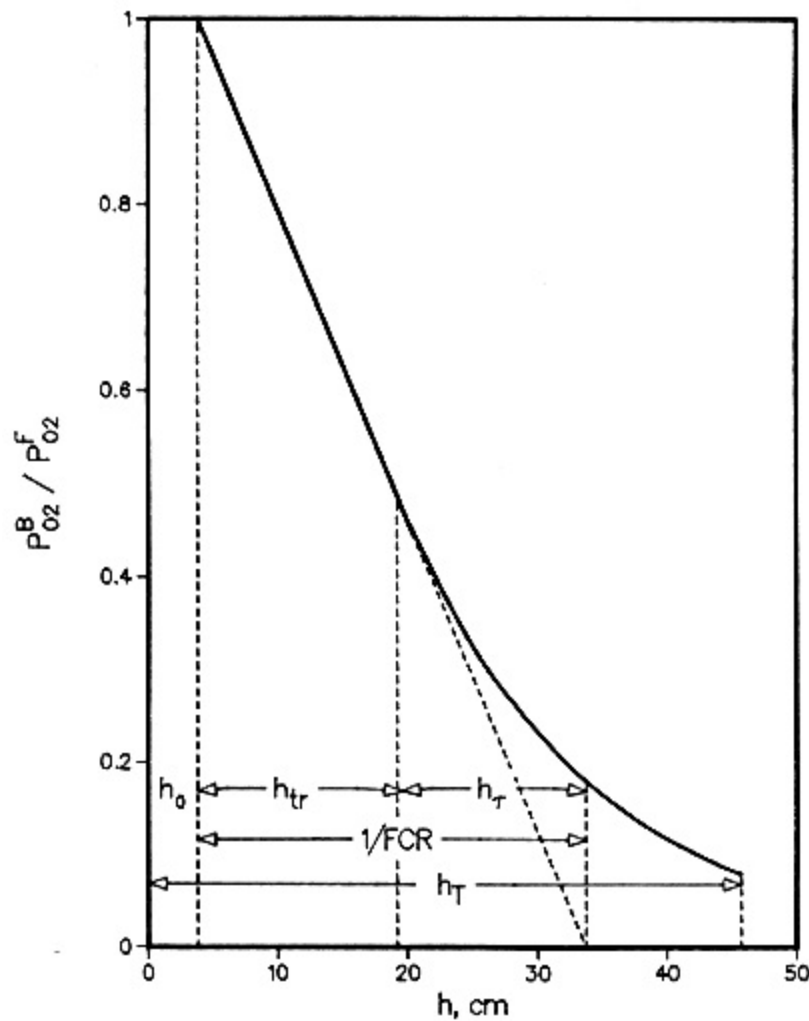


Fig. 3.

Calculated relationship of partial pressure of oxygen in a bubble with liquid column height for Observation 4, Table 1.

breakthrough occurs increases with increasing air rate. In the vicinity of this breakpoint, the reaction becomes very unstable and tends to die.

If one plots the logarithm of the oxygen consumption rate (OCR, calculated from the air rate and the oxygen conversion) vs the reciprocal of the absolute temperature for these data (Arrhenius plot, Fig. 5), a simple interpretation becomes apparent. The plots for the different air rates have a common steep portion with an indicated energy of activation of about 25 kcal/mol. The lines for each air rate deviate from the common segment at individual points and then exhibit low energies of activation. The high energy of activation is exhibited at low temperatures while the low energies of activation are apparent at higher temperatures.

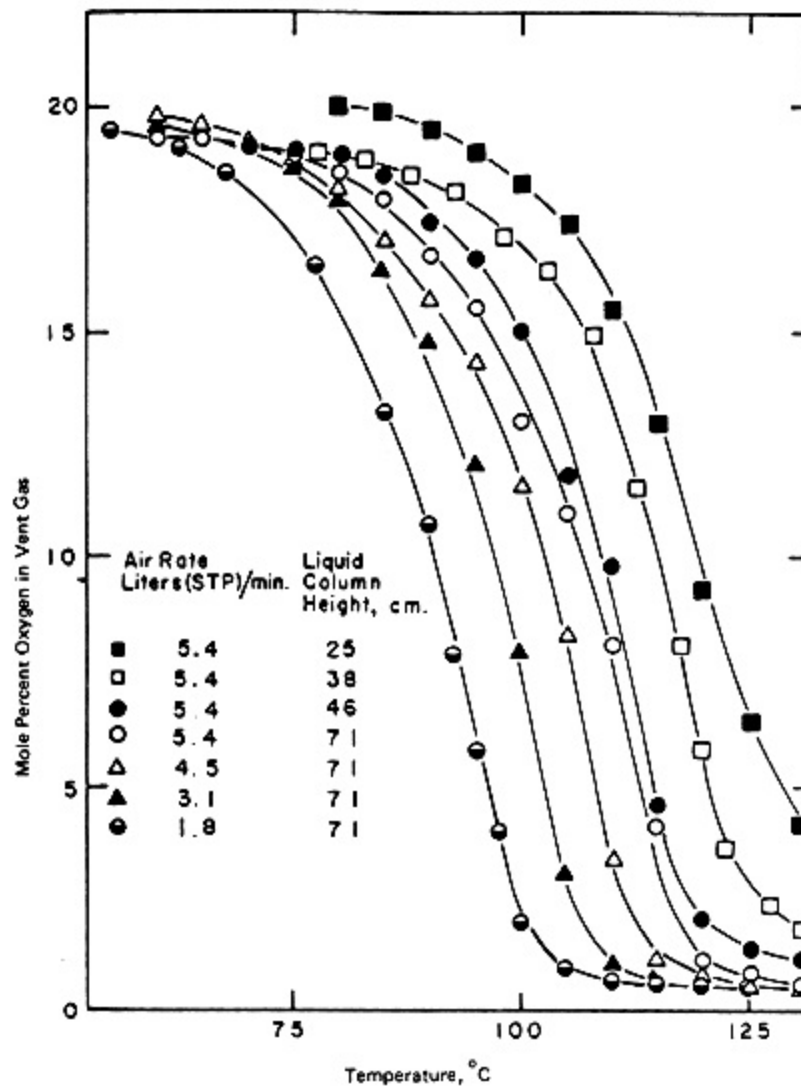


Fig. 4.
Effect of temperature on oxygen concentration in vent gas.

In terms of the ideal reactor discussed above, we expect the system to be mass transfer rate limited (MTRL) at high temperatures and chemically rate limited (CRL) at low temperatures. Autoxidations have been reported to have an overall energy of activation of ~ 25 kcal/mol [10, 28]. Mass transfer, being a physical process, is expected to have an energy of activation of < 5 kcal/mol [29]. As the temperature is increased, the rate of Reaction (2) (and thus the potential rate of Reaction 1) increases faster than the increase of oxygen mass transfer capabilities and, at some point, the system becomes MTRL, even in the vicinity of the sparger. If a reaction operating at high temperature is cooled, the oxygen concentration will increase very little at first. Eventually, a CRLZ will appear around the sparger and begin to ascend the reactor column.

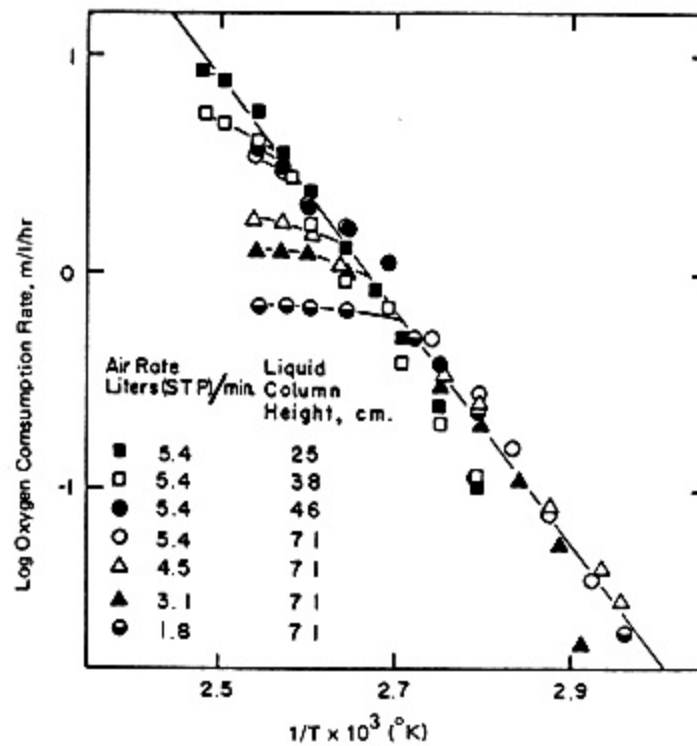


Fig. 5.
Arrhenius plot of oxygen consumption rates.

As the relative size of the CRLZ grows, the oxygen concentration in the vent will increase at an accelerating rate. The reaction will become unstable because the overall energy of activation of the system becomes much greater. A small negative temperature excursion will cause a marked reduction in the reaction rate and, in consequence, a reduction in the heat generation rate. This will lead to a further decrease in temperature and so on. With care, laboratory reactors can be operated under these conditions by designing the system so that the heat of reaction is a relatively small part of the total heat flux. This is not practical in a commercial reactor; the presence of a significant MTRLZ is required for operating stability.

The data from one run shown in Fig. 4 are given in Table 1. An Arrhenius plot of the log OCR vs $1000/T$ is given in Fig. 6. From the steep, straight line portion of this plot, one can calculate the LKR:

$$\text{LKR} = 6.45 \times 10^{10} e^{-24,600/RT} \text{ mmol O}_2/\text{s}/\text{cm}^3 \quad (25)$$

FCRs are calculated from Eq. (22) and (25). Then h_τ can be calculated from a rearrangement of Eq. (23) by using a method of successive approximations. This calculation fails after the first five points because little or no MTRLZ is left. The first five points are in excellent agreement, however, and give $h_\tau = 14.59 \pm 0.20$ cm. The constancy of this value over a range of temperatures indicates that compensating changes are occurring. One expects the diffusion

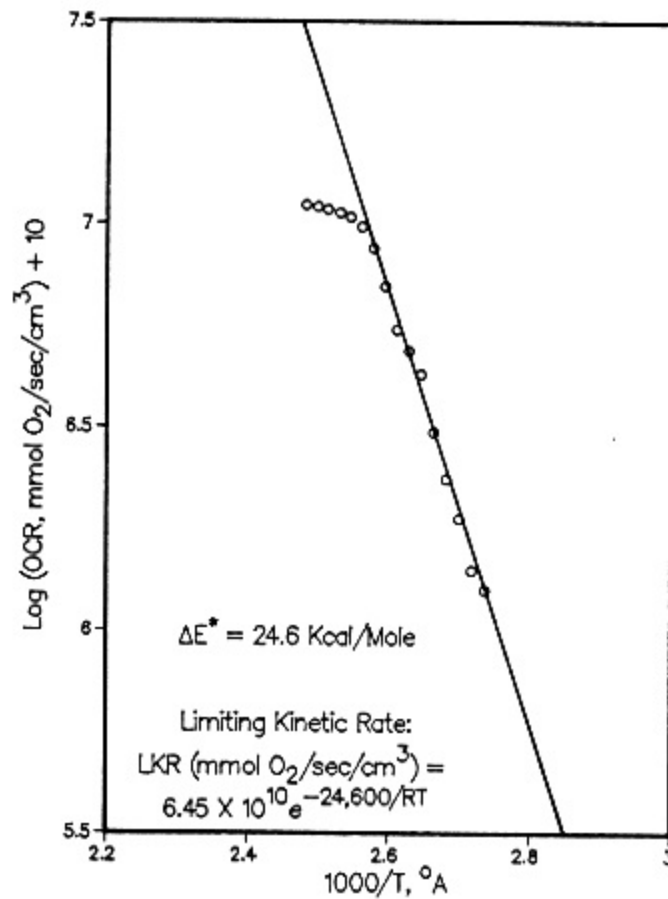


Fig. 6.
Arrhenius plot for methyl ethyl ketone oxidation.
(See Table 1 for data.)

coefficient for oxygen to increase with temperature. It seems likely that higher bubble rise rates, possibly because of higher vapor levels, may be the compensating factor.

Transition height values are calculated from Eq. (24). The percent of the reactor volume in the CRLZ (%V_{CRLZ}) is calculated from

$$\%V_{\text{CRLZ}} = h_{\tau} \times 100 / (h_T - h_0) \quad (26)$$

The percent of the reaction occurring in the CRLZ (%R_{CRLZ}) is calculated from

$$\%R_{\text{CRLZ}} = \text{FCR} \times h_{\tau} \times 100 / \text{FOC} \quad (27)$$

where FOC = fractional oxygen conversion.

Figure 7 is a plot of the observed data with a curve fitted using Eqs. (20) and (21) and a value of $h_{\tau} = 14.59 \text{ cm}$. The good fit probably does not imply

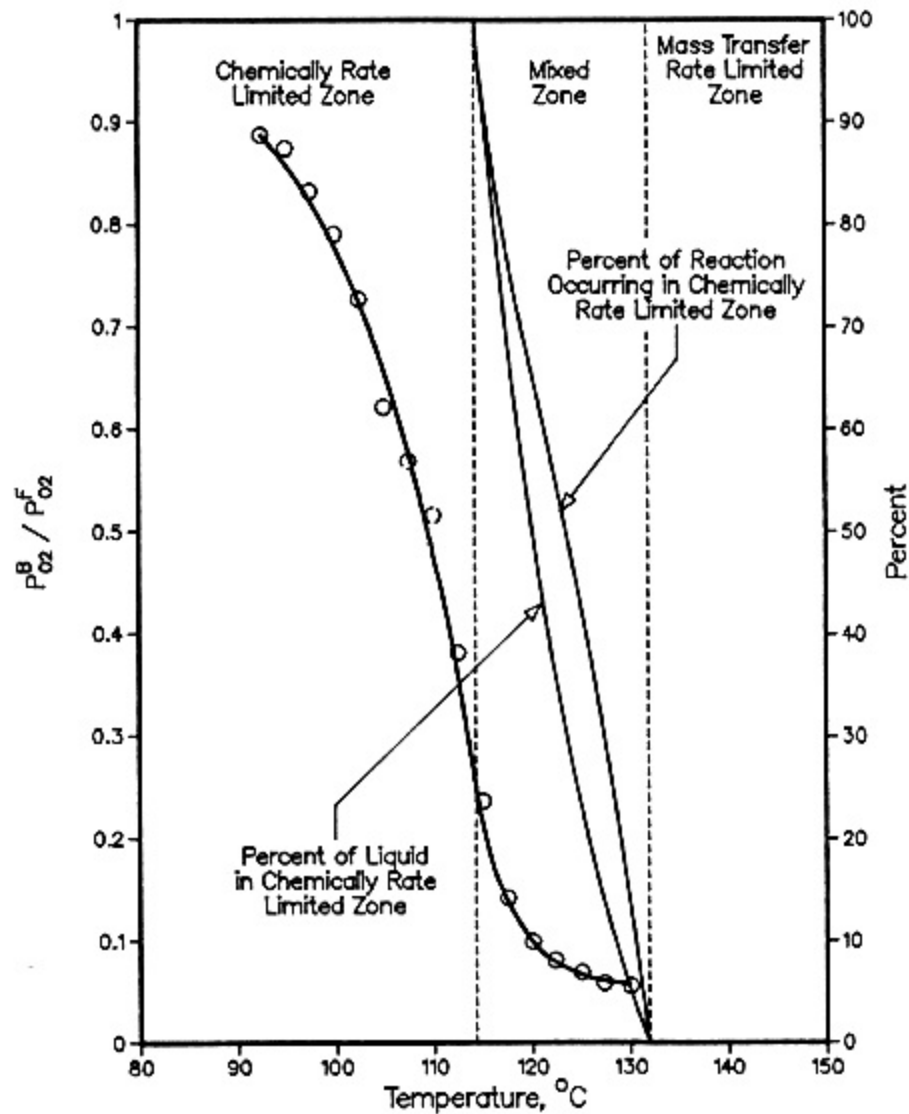


Fig. 7.

Fitted curves for vent gas composition as a function of temperature.
(Data from Table 1.)

any great accuracy for the assumptions but at least indicates the adequacy of the simple model for the present purpose. Also shown in Fig. 7 are the curves for %V_{CRLZ} and %R_{CRLZ}.

Figure 7 indicates that the two-zone interaction which contributes stability to an oxidation reaction can persist until the system is almost 70% chemically rate limited (with almost 80% of the reaction occurring in the CRLZ). It is usually desirable to conduct an oxidation reaction with as much CRLZ as feasible and at as low a temperature as economics allow. This will minimize oxygen starvation loss reactions such as Reaction (13) and bimolecular radical loss reactions such as Reaction (10).

If one has determined a desirable temperature for conducting an oxidation (most likely based on efficiency considerations), it is possible to design a minimum volume reactor for a given air rate by applying the concepts discussed above. For a target oxygen conversion, the number of transfer heights required in a totally MTRL reactor will be given by

$$n = \ln [100/(100 - \text{TOC})] \quad (28)$$

where n = number of MTRL stages required
 TOC = targeted oxygen conversion (%)

It can be shown that the total roused liquid column height required in a mixed zone system is given by

$$h_T - h_0 = 1/\text{FCR} + [n - 1 + \ln (h_r \times \text{FCR})] \times h_r \quad (29)$$

[Equation 29 is only valid for $1/\text{FCR} > h_r$ (required for a mixed zone system).] Utilizing Equation (22), one can show:

$$V = \frac{\text{RF} \times \text{OFR}}{\text{LKR}} \times \left[n - 1 + \ln \left(\frac{h_r \times \text{LKR} \times \text{CSA}}{\text{RF} \times \text{OFR}} \right) \right] \times h_r \times \text{CSA} \quad (30)$$

where V = roused liquid volume (cm^3) above ideal sparger required to achieve targeted oxygen conversion in mixed zone reactor with uniform bubble distribution and uniform CSA.

Starting with an arbitrarily large volume reactor, the required volume will decrease initially as the CSA is decreased. RF will actually increase, but the initial rate of increase will be very low if the initial RF is low (i.e., for low superficial velocity operation). From Eq. (19) and the definition of U_s :

$$\text{RF} = \frac{U_b}{U_b - \frac{\text{VGFR}}{\text{CSA}}} \quad (31)$$

where VGFR = volumetric gas feed rate (cm^3/s). The rate of increase of RF will accelerate as CSA is decreased (since U_s will be increased) until the rising bubbles become so closely packed they begin to interfere with each other. At that point, some bubbles will coalesce and rise faster. This will decrease the rate of RF increase and can even lead to a reduction of RF, depending on specific system rousing behavior [23, 26]. On the other hand, h_r is relatively independent of CSA until the bubbles become closely packed. Past that point, h_r can increase dramatically. The net result is that the required roused liquid reaction volume will go through a minimum as CSA is decreased. The required values of RF and h_r can be determined as a function of superficial gas velocity as discussed above.

The minimum volume reactor so determined may or may not be operable in a practical manner. This is dependent on h_{tr} , which can be evaluated from the following equation

(from Eqs. 22 and 24):

$$h_{tr} = \frac{RF \times OFR}{LKR \times CSA} - h_r \quad (32)$$

If h_{tr} is too large in comparison to reactor diameter, an isolated CRLZ will develop. Since much of it will not be in effective contact with the MTRLZ, the effective energy of activation will be high and the reaction will be unstable. Such reactors frequently develop "cold zones" where the reaction has died and "hot spots" where it is proceeding.

The critical value of h_{tr} /diameter has not been defined; it is probably in the range of 1 to 5 and may well be different in each case. If the value is too large, several options are available. Probably the easiest and most economical approach in the reactor design stage is to increase CSA. This will increase reactor volume somewhat. Another alternative is to increase pressure and thereby decrease RF. This is probably subject to more severe economic limitations. Yet another option is to increase the temperature and thus increase the LKR. One can also reduce OFR, but this gives a proportional cut in productivity. Staging of the oxidant feed by introducing it at multiple levels is a viable alternative which has also been used [30]. In general, tall cylindrical reactors with small diameters are most suitable for reactions with very high LKRs (where h_{tr} s are always near zero; aldehyde oxidations are generally in this category) or reactions whose efficiencies are sufficiently insensitive to temperature to permit acceptable operation at higher temperatures. Most nonaldehyde oxidations are best conducted in reactors with relatively large cross-sectional areas.

Pressure

The role of pressure in LPO is not intuitively apparent. Over the range where rousing factors are independent of superficial gas velocities, i.e., under circumstances where bubbles rise relatively independent of each other, LPOs are remarkably insensitive to pressure. In terms of the simple model discussed here, if the reaction pressure is doubled, the partial pressure of oxygen in the bubbles will be doubled (neglecting vapor pressure) and the mass transfer of oxygen across each unit area of bubble surface will be doubled. The number of bubbles, however, will be halved (since bubble size is largely a function of surface tension) with no net effect on oxygen mass transfer. Other things being equal, pressure begins to have a pronounced effect only when a change in pressure has a significant effect on the rousing factor.

The most important factors in determining desirable reaction pressure are permissible vapor load in the vent gas, how much heat one wishes to remove by vaporization, and the equipment cost for operating at higher pressures.

Symbols

VPO	vapor-phase oxidation
LPO	liquid-phase oxidation

In	inhibitor (free radical consumer or deactivator)
RF	rousing factor (roused liquid volume/true liquid volume)
U_b	bubble rise velocity (cm/s)
U_s	superficial gas velocity (cm/s)
$P_{O_2}^{h_i}$	partial pressure of O_2 at level h_i
$P_{O_2}^B$	partial pressure of O_2 in the bubble (atm)
$P_{O_2}^F$	partial pressure of O_2 in the feed (oxidant) (atm)
$P_{O_2}^V$	partial pressure of O_2 in the vent gas (atm)
h_T	total roused liquid height above sparger (cm)
h_0	height of "ineffective" zone above sparger where bubbles are forming
h_i	height of point i in liquid column above h_0
h_τ	transfer height (cm); the vertical distance over which a bubble delivers ~63% of its oxygen to the liquid in a MTRLZ
h_{tr}	transition height (cm); the height of the interface between the MTRLZ and the CRLZ above h_0
MTRLZ	mass transfer rate limited zone; rate of oxygen consumption is first order with respect to $P_{O_2}^B$
CRLZ	chemically rate limited zone; rate of oxygen consumption is zero order with respect to $P_{O_2}^B$
LKR	limiting kinetic rate; the rate of oxygen consumption (mmol/s/cm ³) in the CRLZ
FCR	fractional chemical rate; the fraction of the total oxygen feed rate which is consumed in a vertical 1 cm zone in the CRLZ
CSA	cross-sectional area of oxidation reactor (cm ²)
OCR	average oxygen consumption rate in active reaction zone (mmol O_2 /s/cm ³)
OFR	oxidant feed rate (mmol O_2 /s)

FOC fractional oxygen conversion
 TOC targeted oxygen conversion (%)

n number of MTRLZ stages ($h\tau$ units high) required to achieve TOC in a completely MTRL reaction zone

VGFR volumetric gas feed rate (cm^3/s) at reaction conditions

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Petroleum Processing

Harold L. Hoffman
and John J. McKetta

The world presently gets most of its energy from crude oil and natural gas. Petroleum is the major source of fuel used in transportation, manufacturing, and home heating.

Primary energy sources are defined as those coming from natural raw materials. The primary energy sources for the world during 1979 are reported [1] in Fig. 1. Oil and gas together furnished 65% of the total world energy usage for that year.

Note electricity is missing from this representation. Electricity is a secondary energy source because it is generated by consuming some of the other natural resources shown in Fig. 1. Thus, electricity should not appear in an energy balance unless the fuel from which it is generated is omitted from the other totals. Too often, this correction is not made and an inflated energy supply results.

World proven crude oil reserves determined for several earlier years [2] are shown in Table 1. Also included in this table are the annual production rates [3] and the ratio of the reserves to annual production.

What is disturbing at present is the fact that new oil sources are not being found fast enough to keep up with rapidly growing consumption rates. Furthermore, when oil is found, it is generally at greater depths or under seabeds farther from shore than was the case before. Reports proliferate now regarding the ultimate reserves likely to be found in the world.

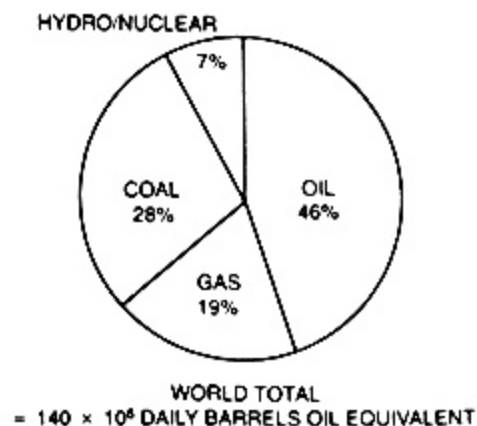


Fig. 1.
World energy consumption, 1979. World total equals 140×10^6 daily barrels oil equivalent.

TABLE 1 World Proven Crude Oil Reserves Compared with Production Rates (109 barrels)

Year	Proven Reserves, First of Year [2]	Annual Production [3]	Ratio, Reserves Divided by Production, Years
1935	23.4	1.65	14.2
1940	34.9	2.15	16.2
1945	51.2	2.59	19.8
1950	76.4	3.80	20.1
1955	153.7	5.63	27.3
1960	255.8	7.67	33.4
1965	341.7	11.06	30.9
1970	516.7	16.69	31.0
1975	569.1	19.50	29.2
1980	625.8	22.4	28.4
1985	696.3	20.36	34.11
1986	692.8	20.15	34.38

Ultimate recoverable petroleum reserves have been estimated with wide variations, the consensus being between 1.5 to 2.5 trillion barrels (10¹² bbl). Most estimators go to great length to explain the basis of their estimates. By comparison, proven reserves are in the neighborhood of 600 billion barrels. Proven reserves are generally taken to mean: "the oil remaining in the ground which geological and engineering information indicate with reasonable certainty to be recoverable in the future from known reservoirs under existing economic and operating conditions" [2].

Alternate feedstocks for refineries are being sought from coal, tar sands, and shale oil. Synthetic crude oil will be made from these raw materials so that conventional refining units can continue to be used to make consumer products.

In the meantime, top priority will be given to use crude oil to make liquid transportation fuels (because of their convenience) and petrochemical materials (because of their diversity of uses). It's a good bet that many of the gross conversion methods now applied to crude oil processing will be replaced in the future by more specific conversion. It is in this transition that knowledge of organic chemistry guides the development of new refining processes.

From Well to Refinery

A country-by-country listing [1] of crude oil production and consumption shows the importance of petroleum movement around the world. Production and demand rates of crude oil for various countries are shown in Table 2.

TABLE 2 Worldwide Petroleum Production and Demand for 1985 (thousands of barrels per day)^a

Continent ^b and Country ^c	Production ^d	Demand	Production-Demand Ratio
North America, total	14,892	16,640	0.89
Canada	1,568	1,470	1.07
Mexico	2,703	e	
United States	10,621	15,170	0.70
South America, total	3,623	4,430	0.82
Argentina	460	e	
Brazil	563	e	
Colombia	176	e	
Trinidad and Tobago	185	e	
Venezuela**	1,693	e	
Other South America	546	e	
Eastern Europe, total*	12,344	11,610	1.06
USSR	11,982	9,060	1.32
Other Eastern Europe	362	2,550	0.14
Western Europe, total	3,731	11,950	0.31
France	53	1,785	0.03
Germany, West	81	2,410	0.03
Italy	44	1,745	0.03
Netherlands	72	640	0.11
Norway	803	190	4.23
United Kingdom	2,444	1,635	1.49
Other Western Europe	234	3,545	0.07
Africa, total	5,284	1,715	3.08
Algeria**	980	e	
Egypt	895	e	
Libya**	1,050	e	
Nigeria**	1,480	e	
South Africa	e	e	
Other Africa	879	e	
Middle East, total	10,580	1,980	5.34
Iran**	2,258	e	
Iraq**	1,436	e	
Kuwait**	939	e	
Saudi Arabia**	3,255	e	
Other Middle East	2,692	e	
Far East, total	6,958	10,140	0.69
Australia and New Zealand	597	670	0.89
Brunei and Malaysia	1,830	e	
China*	2,498	1,760	1.42
India	606	e	
Indonesia**	1,315	e	
Japan	10	4,320	0.00
Other Far East	102	e	
Total world	57,412	58,465	0.98
Communist controlled countries*	14,842	13,370	1.11
OPEC countries**	14,406	e	

^aAuthority: United States Department of Energy; BP Statistical Review of World Energy, June 1985; World Oil; Statistics Canada.

bContinent totals may include countries not identified.
cCommunist controlled countries are identified by a single asterisk; OPEC countries by a double asterisk.
dWhen available, figures include natural gas liquids production.
eData not available.

The growth of world refining capacity attempts to keep up with the growing demand for petroleum products. A measure of this growth is shown in Fig. 2. The upper curve shows total refining capacity, while the lower curve shows the amount of crude oil run through the refineries.

One might wonder why refining capacity continued to surge ahead when crude throughput took a dip in the period from 1974 through 1976. For one thing, the amount of crude oil available for processing is subject to the whims of international trade. Since so much crude oil comes from some countries (notably, Middle Eastern countries) to be refined in other countries, international relations between countries are a strong factor that determines how much crude oil feedstock is available.

Another factor in refining growth is the time required to construct processing units. In highly industrialized countries like the United States, Japan, and Western European countries, there are mounting restrictions on new refinery sites. Thus, a decision to build a refinery and the actual completion of that refining capacity will take several years in order to fulfill local and governmental requirements. Then one to four years of actual construction activities are required before a new refinery will start processing feedstocks.

Refineries are located mostly in the countries consuming refined products. It is easier to transport crude oil to major refining centers than to transport separately the many individual products. The distribution of refining capacity [1] by areas for 1980 is depicted in Fig. 3.

The variety of ways crude oils are delivered to refineries is indicated by using United States refineries as an example. United States refineries get their feedstock via pipelines, tank trucks, barges, and ocean-going vessels [4]. The amount received by each of these routes is shown in Table 3. The large quantity coming by water explains why many refineries are located near oceans and why they own or lease such as large fleet of barges and ocean-going vessels.

Product Names

The distinction between refined products and petrochemicals is often a subtle one. In general, when the product is a fraction from crude oil that includes a fairly large group of hydrocarbons, the fraction is classified as a refined product. Examples of refined products are: gasoline, diesel fuel, heating oils, lubricants, waxes, asphalts, and petroleum coke.

By contrast, when the product from crude oil is limited to only one or two specific hydrocarbons of fairly high purity, the fraction is called a petrochemical. Examples of petrochemicals are: ethylene, propylene, benzene, toluene, and styrene to name only a few.

There are many more identifiable petrochemical products than there are refined products. There are many specific hydrocarbons that can be derived from petroleum. However,

these hydrocarbons lose individual identity when they are grouped into a refined product.

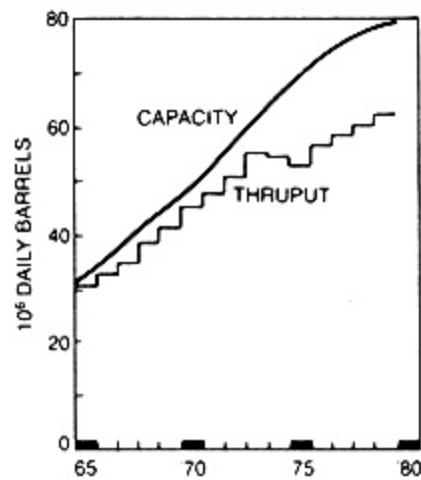


Fig. 2.
World refining capacity and crude oil throughputs.

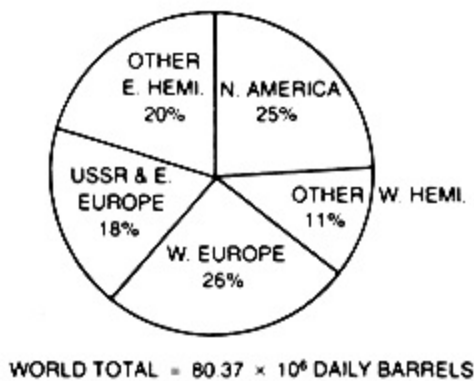


Fig. 3.
World refining capacity in early 1980.

TABLE 3 Method of Transportation for Crude Oil Received by United States Refineries, 1979 [4]

Transportation Method	Vol. %
Domestic crude oil:	
Pipelines	42.9
Tank cars and trucks	2.1
Tankers and barges	11.0
Subtotal	56.0
Foreign crude oil:	
Pipelines	12.7
Tankers and barges	31.3
Subtotal	44.0
Total receipts	100.0

Refined Products

Most refined products at the consumer level are blends of several refinery streams. Product specifications determine which streams are suitable for a specific blend. Part of the difficulty of learning about refining lies in the industry's use of stream names that are different from the names of the consumer products.

Consider the listing in Table 4. The names in the last column should be familiar because they are used at the consumer level. Yet within a refinery, these products will be blended from portions of crude oil fractions having the names shown in the first column. To make matters worse, specifications and statistics for the industry are often reported under yet another set of names those shown in the middle column of Table 4.

Gasoline at the consumer level, for example, may be called benzol or petrol, depending on the country where it is sold. In the early stages of crude oil processing, most gasoline components are called naphthas. Kerosene is another example. It may be called coal oil to denote that it replaces stove oil (or range oil) once derived from coal. Kerosene's historical significance was first as an illuminating oil for lamps that once burned sperm oil taken from whales. But today, kerosene fractions go mostly into transportation fuels such as jet fuel and high quality No. 1 heating oil.

Product Specifications

Product application and customer acceptance set detailed specifications for various product properties. In the United States, the American Society for Testing and Materials (ASTM) and the American Petroleum Institute (API) are recognized for establishing specifications on both products and methods for testing. Other countries have similar referee organizations. For example,

TABLE 4 Several Names for the Same Material

Crude Oil Cuts	Refinery Blends	Consumer Products
Gases	Still gases	Fuel gas
	Propane/butane	Liquefied petroleum gas (LPG)
Light/heavy naphtha	Motor fuel	Gasoline
	Aviation turbine, Jet-B	Jet fuel (naphtha type)
Kerosene	Aviation turbine, Jet-A	Jet fuel (kerosene type)
	No. 1 fuel oil	Kerosene (range oil)
Light gas oil	Diesel	Auto and tractor diesel
	No. 2 fuel oil	Home heating oil
Heavy gas oil	No. 4 fuel oil	Commercial heating oil
	No. 5 fuel oil	Industrial heating oil
	Bright stock	Lubricants
Residuals	No. 6 fuel oil	Bunker C oil
	Heavy residual	Asphalt
	Coke	Coke

in the United Kingdom, it is the Institute of Petroleum (IP). In West Germany, it is Deutsches Institute fuer Normung (DIN). In Japan, it is the Ministry of International Trade and Industry (MITI).

Boiling range is the major distinction among refined products, and many other properties are related directly to the products in these boiling ranges. A summary of ASTM specifications for fuel boiling ranges [5] is given in Table 5.

TABLE 5 Major Petroleum Products and Their Specified Boiling Range [5]

Product Designation	ASTM Designation	Specified Temperature for vol.% Distilled at 1 atm (°F)		
		10	50	90
Liquefied petroleum gas (LPG):	D1835			
Commercial propane		a		b
Commercial butane		a		c
Aviation gasoline (Avgas)	D910	158 max	221 max	275 maxd
Automotive gasoline:	D439			
Volatility class A		158 max	170250	374 maxe
Volatility class B		149 max	170245	374 maxe
Volatility class C		140 max	170240	365 maxe
Volatility class D		131 max	170235	365 maxe
Volatility class E		122 max	170230	365 maxe
Aviation turbine fuel:	D1655			
Jet A or A-1		400 max		f
Jet B		g	370 max	470 max
Diesel fuel oil:	D975			
Grade 1-D				550 max
Grade 2-D				540640
Grade 4-D			Not specified	
Gas turbine fuel oil:	D2880			
No. 0-GT			Not specified	
No. 1-GT				550 max
No. 2-GT				540640
No. 3-GT			Not specified	
No. 4-GT			Not specified	
Fuel oil:	D396			
Grade No. 1		420 max		550 max
Grade No. 2		h		540640
Grade No. 4			Not specified	
Grade No. 5			Not specified	
Grade No. 6			Not specified	

aVapor pressure specified instead of front end distillation.

b95% point, -37°F max.

c95% point, 36°F max.

dFinal point, 338°F max.

eFinal point, all classes, 437° F max.

fFinal point, 572°F max.

g20% point, 290°F max.

hFlash point specified instead of front end distillation.

Boiling range also is used to identify individual refinery streams as an example will show in a later section concerning crude oil distillation. The temperature that separates one fraction from an adjacent fraction will differ from refinery to refinery. Factors influencing the choice of cut point temperatures includes the following: type of crude oil feed, kind and size of down-stream processes, and relative market demand among products.

Other specifications can involve either physical or chemical properties. Generally these specifications are stated as minimum or maximum quantities. Once a product qualifies to be in a certain group, it may receive a premium price by virtue of exceeding minimum specifications or by being below maximum specifications. Yet all too often, the only advantage for being better than specifications is an increase in the volume of sales in a competitive market.

The evolution of product specifications will, at times, appear sadly behind recent developments in more sophisticated analytical techniques. Certainly the ultimate specifications should be based on how well a product performs in use. Yet the industry has grown comfortable with certain comparisons, and these standards are retained for easier comparison with earlier products. Thus, it is not uncommon to find petroleum products sold under an array of tests and specifications some seemingly measuring similar properties.

It is behind the scenes that sophisticated analytical techniques prove their worth. These techniques are used to identify specific hydrocarbons responsible for one property or another. Then suitable refining processes are devised to accomplish a desired chemical reaction that will increase the production of specific types of hydrocarbons.

In the discussion on refining schemes, major specifications will be identified for each product category. It will be left to the reader to remember that a wide variety of other specifications also must be met.

Product Yields

As changes occur in relative demand for refined products, refiners turn their attention to ways that will alter internal refinery streams. The big problem here is that the increase in volume of one fraction of crude oil will deprive some other product of that same fraction. This point is often overlooked when the question arises: "How much of a specific product can a refinery make?" Such a question should always be followed by a second question: "What other products will be penalized?"

Envision, for example, what would happen if the refining industry were to make all the gasoline it possibly could with today's present technology. The result would be to rob many other petroleum products. A vehicle which needs gasoline for fuel also needs such products as industrial fuels to fabricate the vehicle, lubricants for the engine's operation, asphalt for roads upon which the vehicle is to move, and petrochemical plastics and fibers for the vehicle's interior. Until adequate substitutes are found for these other petroleum

products, it would be unwise to make only one product, even though sufficient technology may exist to offer this option.

TABLE 6 Product Yields from United States
Refineries, 1986 [4]

Product	Vol.% of Refinery Input
Still gas	4.0
Ethane/ethylene	0.1
Liquefied gas	2.4
Gasoline	42.1
Jet fuel	7.4
Kerosene	1.6
Special naphtha	0.8
Petrochemical feed	4.4
Distillates	20.9
Lubricants	1.2
Waxes	0.1
Coke	2.3
Asphalt	3.0
Road oil	0.1
Residuals	11.8
Miscellaneous	0.8
Total	110.4a

aIncludes 10.4% vol. % gain because most products are of less density than original feedstock.

This is not to say that substitutes will not be found nor that these substitutes will not be better than petroleum products. In fact, many forecasts suggest that petroleum will ultimately be allocated only to transportation fuels and petrochemical feedstocks. It appears that these uses are the most suitable options for petroleum crude oil.

In the United States, the relative portions of refined products [4] made from crude oil are shown in Table 6. This distribution of products is the result of a long-standing trend to convert the heavier less valuable fractions into lighter, more valuable fractions. The ways this can be done will be discussed in the section on refinery schemes.

Petrochemicals

The portion of crude oil going to petrochemicals may appear small compared to fuels, but the variety of petrochemicals is huge. The listing in Table 7 will give some idea of the range of petrochemical applications.

Despite their variety, all commercially manufactured petrochemicals account for the consumption of only a small part of the total crude oil processed. In the United States, where petrochemicals have grown swiftly, the total petrochemical output at the beginning of 1980 was little more than 6 1/2 vol.% of all petroleum feedstocks. An estimated 2 1/2 vol.% went to energy of

TABLE 7 Petrochemical Applications

Absorbents	De-emulsifiers	Hair conditioners	Pipe
Activators	Desiccants	Heat transfer fluids	Plasticizers
Adhesives	Detergents	Herbicides	Preservatives
Adsorbents	Drugs	Hoses	Refrigerants
Analgesics	Drying oils	Humectants	Resins
Anesthetics	Dyes	Inks	Rigid foams
Antifreezes	Elastomers	Insecticides	Rust inhibitors
Antiknocks	Emulsifiers	Insulations	Safety glass
Beltings	Explosives	Lacquers	Scavengers
Biocides	Fertilizers	Laxatives	Stabilizers
Bleaches	Fibers	Odorants	Soldering flux
Catalysts	Films	Oxidation inhibitors	Solvents
Chelating agents	Finish removers	Packagings	Surfactants
Cleaners	Fire-proofers	Paints	Sweeteners
Coatings	Flavors	Paper sizings	Synthetic rubber
Containers	Food supplements	Perfumes	Textile sizings
Corrosion inhibitors	Fumigants	Pesticides	Tire cord
Cosmetics	Fungicides	Pharmaceuticals	
Cushions	Gaskets	Photographic chemicals	

conversion, leaving 4 vol.% represented as petrochemical products. Even so, this quantity has been sufficient for petrochemical-based materials to replace many products once made from such raw materials as coal, lumber, metal ores, and so forth.

Refining Schemes

A refinery is a massive network of vessels, equipment, and pipes. The total scheme can be divided into a number of unit processes. In the discussion to follow, only major flow streams will be shown, and each unit will be depicted by a single block on a simplified flow diagram. Details will be discussed later.

Refined products establish the order in which each refining unit will be introduced. Only one or two key product specifications are used to explain the purpose of each unit. Nevertheless, the reader is reminded that the choice from among several types of units and the size of these units are complicated economic decisions. The trade-off among product types, quantity, and quality will be mentioned to the extent that they influence the choice of one kind of process unit over another.

Feedstock Identification

Each refinery has its own range of preferred crude oil feedstock for which a desired distribution of products is obtained. The crude oil usually is identified

by its source country, underground reservoir, or some distinguishing physical or chemical property. The three most frequently specified properties are density, chemical characterization, and sulfur content.

API gravity is a contrived measure of density [6]. The relation of API gravity to specific gravity is given by

$$^{\circ}\text{API} = \frac{141.5}{\text{sp gr}} - 131.5$$

where sp gr is the specific gravity, or the ratio of the weight of a given volume of oil to the weight of the same volume of water at a standard temperature, usually 60°F.

An oil with a density the same as that of water, or with a specific gravity of 1.0, would then be 10°API oil. Oils with higher than 10°API gravity are lighter than water. Since lighter crude oil fractions are usually more valuable, a crude oil with a higher °API gravity will bring a premium price in the market place.

Heavier crude oils are getting renewed attention as supplies of lighter crude oil dwindle. In 1967 the U.S. Bureau of Mines (now part of the U.S. Department of Energy) defined heavy crudes as those of 25°API or less. More recently, the American Petroleum Institute proposed to use 20°API or less as the distinction for heavy crude oils.

A characterization factor was introduced by Watson and Nelson [7] to use as an index of the chemical character of a crude oil or its fractions. The Watson characterization factor is defined as follows:

$$\text{Watson } K = (T_B)^{1/3} / \text{sp gr}$$

where T_B is the absolute boiling point in degrees Rankin and sp gr is specific gravity compared to water at 60°F. For a wide boiling range material like crude oil, the boiling point is taken as an average of the five temperatures at which 10, 30, 50, 70, and 90% is vaporized.

A highly paraffinic crude oil might have a characterization factor as high as 13 while a highly naphthenic crude oil could be as low as about 10.5. Highly paraffinic crude oils can also contain heavy waxes which make it difficult for the oil to flow. Thus, another test for paraffin content is to measure how cold a crude oil can be before it fails to flow under specific test conditions. The higher the pour point temperature, the greater the paraffin content for a given boiling range.

Sour and sweet are terms referring to a crude oil's approximate sulfur content. In early days, these terms designated smell. A crude oil with a high sulfur content usually contains hydrogen sulfide the gas associated with rotten eggs. Then the crude oil was called sour. Without this disagreeable odor, the crude oil was judged sweet. Today, the distinction between sour and sweet is based on total sulfur content. A sour crude oil is one with more than 0.5 wt.% sulfur, whereas a sweet crude oil has 0.5 wt.% or less sulfur. It has

been estimated that 58% of United States crude oil reserves are sour. More importantly, an estimated 81% of world crude oil reserves are sour [8].

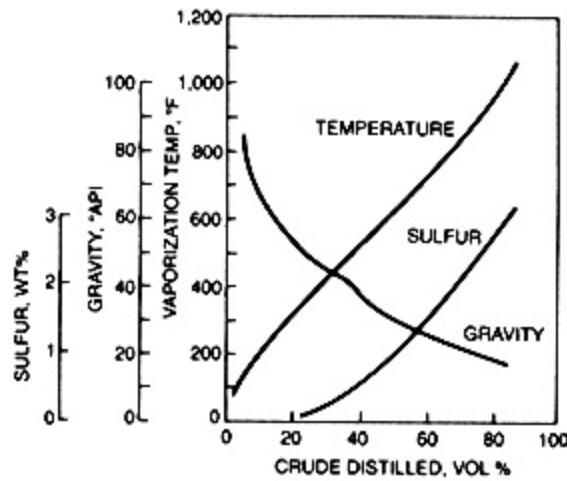


Fig. 4.
Analysis of Light Arabian crude oil.

ASTM distillation is a test prescribed by the American Society for Testing and Materials to measure the volume percent distilled at various temperatures [5]. The results are often reported the other way around: the temperatures at which given volume percents vaporize [9]. These data indicate the quantity of conventional boiling range products occurring naturally in the crude oil. Analytical tests on each fraction indicate the kind of processing that may be needed to make specification products. A plot of boiling point, sulfur content, and API gravity for fractions of Light Arabian crude oil are shown in Fig. 4. This crude oil is among the ones most traded in the international crude oil market.

In effect, Fig. 4 shows that the material in the mid-volume range of Light Arabian crude oil has a boiling point of approximately 600°F, a liquid density of approximately 30°API, and an approximate sulfur content of 1.0 wt.%. These data are an average of eight samples of Light Arabian crude oil. More precise values would be obtained on a specific crude oil if the data were to be used in design work.

Since a refinery stream spans a fairly wide boiling range, the crude oil analysis data would be accumulated throughout that range to give fraction properties. The intent here is to show an example of the relation between volume distilled, boiling point, liquid density, and sulfur content.

Crude Oil Pretreatment

Crude oil comes from the ground admixed with a variety of substances: gases, water, and dirt (minerals). The technical literature devoted to petroleum refining often omits crude oil clean-up steps. It is likely presumed that the reader wishing to compare refining schemes will understand that the crude has already been through these clean-up steps. Yet cleanup is important if the

crude oil is to be transported effectively and to be processed without causing fouling and corrosion. Cleanup takes place in two ways: field separation and crude desalting.

Field separation is the first attempt to remove the gases, water, and dirt that accompany crude oil coming from the ground. As the term implies, field separation is located in the field near the site of the oil wells. The field separator is often no more than a large vessel which gives a quieting zone to permit gravity separation of three phases: gases, crude oil, and water (with entrained dirt).

The crude oil is lighter than water but heavier than the gases. Therefore, crude oil appears within the field separator as a middle layer. The water is withdrawn from the bottom to be disposed of at the well site. The gases are withdrawn from the top to be piped to a natural gas processing plant or are pumped back into the oil well to maintain well pressure. The crude oil from the middle layer is pumped to a refinery or to storage awaiting transportation by other means.

Crude desalting is a water-washing operation performed at the refinery site to get additional crude oil cleanup [10]. The crude oil coming from field separators will continue to have some water and dirt entrained with it. Water washing removes much of the water-soluble minerals and entrained solids.

If these crude oil contaminants were not removed, they would cause operating problems during refinery processing. The solids (dirt and silt) would plug equipment. Some of the solids, being minerals, would dissociate at high temperature and corrode equipment. Still others would deactivate catalysts used in some refining processes.

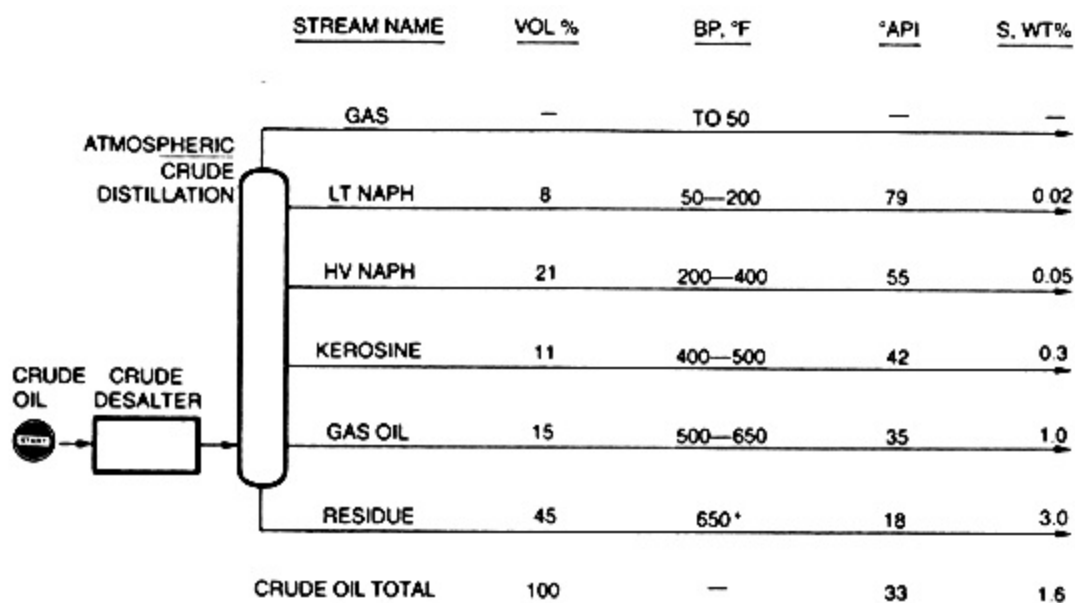


Fig. 5.
Separating desalted crude oil into fractions.

Crude Oil Fractions

The importance of boiling range for petroleum products has already been discussed in connection with the earlier Table 5. The simplest form of refining would isolate crude oil into fractions having boiling ranges that would coincide with the temperature ranges for consumer products. Some treating steps might be added to remove or alter undesirable components, and a very small quantity of various chemical additives would be included to enhance final properties.

Crude oil distillation separates the desalted crude oil into fractions of differing boiling ranges. Instead of trying to match final product boiling ranges at this point, the fractions are defined by the number and kind of downstream processes.

The desalting and distillation units are depicted in Fig. 5 to show the usual fractions coming from crude oil distillation units. The discussion in the following paragraphs shows the relationships between some finished products and downstream processing steps.

Gasoline

The light and heavy naphtha fractions from crude oil distillation are ultimately combined to make gasoline. The two streams are isolated early in the refining scheme so that each can be refined separately for optimum blending in order to achieve required specifications of which only volatility, sulfur content, and octane number will be discussed.

Volatility

A gasoline's boiling range is important during its aspiration into the combustion chamber of a gasoline-powered engine. Vapor pressure, a function of the fuel's boiling range, is also important. Boiling range and vapor pressure are lumped into one concept, volatility [11].

Lighter components in the gasoline blend are established as a compromise between two extremes: enough light components are needed to give adequate vaporization of the fuel-air mixture for easy engine starting in cold weather, but too much of the light components can cause the fuel to vaporize within the fuel pump and result in vapor lock.

Heavier components are a trade-off between fuel volume and combustion chamber deposits. Heavier components extend the yield of gasoline that can be made from a given volume of crude oil. But heavier components also contribute to combustion chamber deposits and spark plug fouling. Thus, an upper limit is set on gasoline's boiling range to give a clean-burning fuel.

Sulfur Content

Sulfur compounds are corrosive and foul smelling. When burned in an engine, these compounds result in sulfur dioxide exhaust. Should the engine be equipped with a catalytic muffler, as is the case for many modern automobile engines, the sulfur is exhausted from the muffler as sulfur trioxide, or sulfuric acid mist.

Caustic wash or some other enhanced solvent washing technique is usually sufficient to remove sulfur from light naphtha. The sulfur compounds in light naphtha are mercaptans and organic sulfides that are removed readily by these washing processes.

Heavy naphtha is harder to desulfurize. The sulfur compounds are in greater concentration and are of more complicated molecular structure. A more severe desulfurization method is needed to break these structures and release the sulfur. One such process is hydrotreating.

Hydrotreating is a catalytic process that converts sulfur-containing hydrocarbons into low-sulfur liquids and hydrogen sulfide [12]. The process is operated under a hydrogen-rich blanket at elevated temperature and pressure. A separate supply of hydrogen is needed to compensate for the amount of hydrogen required to occupy the vacant hydrocarbon site once held by the sulfur. Also, hydrogen is consumed to convert the sulfur to hydrogen sulfide gas.

Nitrogen and oxygen compounds are also dissociated by hydrotreating. The beauty of the process is that molecules are split at the points where these contaminants are attached. For nitrogen and oxygen compounds, the products of hydrotreating are ammonia and water, respectively. Thus, the contaminants will appear in the off-gases and are easily removed by conventional gas treating processes.

Octane Number

Another condition to keep gasoline engines running smoothly is that the fuel-air mixture start burning at a precise time in the combustion cycle. An electrical spark starts the ignition. The remainder of the fuel-air mix should be consumed by a flame front moving out from the initial spark.

Under some conditions, a portion of fuel-air mixture will ignite spontaneously instead of waiting for the flame front from the carefully timed spark. The extra pressure pulses resulting from spontaneous combustion are usually audible above the normal sounds of a running engine and give rise to the phenomenon called "knock." Some special attributes of the knocking phenomenon are called pinging and rumble. All of these forms of knock are undesirable because they waste some of the available power of an otherwise smooth-running engine.

Octane number is a measure of a fuel's ability to avoid knocking. The octane number of a gasoline is determined in a special single cylinder engine where various combustion

conditions can be controlled [5]. The test engine is

adjusted to give trace knock from the fuel to be rated. Then various mixtures of isooctane (2,2,4-trimethyl pentane) and normal heptane are used to find the ratio of the two reference fuels that will give the same intensity of knock as that from the unknown fuel. Defining isooctane as 100 octane number and normal heptane as 0 octane number, the volumetric percentage of isooctane in heptane that matches knock from the unknown fuel is reported as the octane number of the fuel. For example, 90 vol.% isooctane and 10 vol.% normal heptane establishes a 90 octane number reference fuel.

Two kinds of octane number ratings are specified, although other methods are often used for engine and fuel development. Both methods use the same reference fuels and essentially the same test engine. Engine operating conditions are the difference. In one, called the Research method, the spark advance is fixed, the air inlet temperature is 125°F, and engine speed is 600 r/min. The other, called the Motor method, uses variable spark timing, a higher mixture temperature (300°F), and a faster engine speed (900 r/min).

The more severe conditions of the Motor method have a greater influence on commercial blends than they do on the reference fuels. Thus, a Motor octane number of a commercial blend tends to be lower than the Research octane number. Recently, it has become the practice to label gasoline with an arithmetic average of both ratings, abbreviated (R+M)/2.

Catalytic reforming is the principal process for improving the octane number of a naphtha for gasoline blending [10]. The process gets its name from its ability to re-form or re-shape the molecular structure of a feedstock. The transformation that accounts for the improvement in octane number is the conversion of paraffins and naphthenes to aromatics. The aromatics have better octane numbers than their paraffin or naphthene homologs. The greater octane number increase for the heavier molecules explains why catalytic reforming is usually applied to the heavy naphtha fractions.

Catalysts for reforming typically contain platinum or a mixture of platinum and other metal promoters on a silica-alumina support. Only a small concentration of platinum is used, averaging about 0.4 wt.%. The need to sustain catalyst activity and the expense of the platinum make it common practice to pretreat the reformer's feedstock to remove catalyst poisons.

Hydrotreating, already discussed, is an effective process to pretreat reforming feedstocks. The two processes go together well for another reason. The reformer is a net producer of hydrogen by virtue of its cyclization and dehydrogenation reactions. Thus, the reformer can supply the hydrogen needed by the hydrotreating reactions. A rough rule-of-thumb is that a catalytic reformer produces 800-1200 SCF of hydrogen per barrel of feed, while the hydrotreater consumes about 100-200 SCF/bbl for naphtha treating. The excess hydrogen is available for hydrotreating other fractions in separate hydrotreaters [13].

Distillates

Jet fuel, kerosene (range oil), No. 1 fuel oil, No. 2 fuel oil, and diesel fuel are all popular distillate products coming from 400 to 600°F fractions of crude oil.

One grade of jet fuel uses the heavy naphtha fraction, but the kerosene fraction supplies the more popular heavier grade of jet fuel, with smaller amounts sold as burner fuel (range oil) or No. 1 heating oil.

Some heating oil (generally No. 2 heating oil) and diesel fuel are very similar and are sometimes substitutes for each other. The home heating oil is intended to be burned within a furnace for space heating. The diesel fuel is intended for compression-ignition engines.

Hydrotreating improves the properties of all these distillate products. The process not only reduces the sulfur content of the distillates to a low level but also hydrogenates unsaturated hydrocarbons so that they will not contribute to smoke and particulate emissions whether the fuel is burned in a furnace or used in an engine.

Residuals

Crude oil is seldom distilled at temperatures above about 650°F. At higher temperatures, coke will form and plug the lower section of the crude oil distillation tower. Therefore, the portion with a boiling point above 650°F is not vaporized or at least not with the processing units introduced so far. This residual liquid is disposed of as industrial fuel oils, road oils, etc. The residual is sometimes called reduced crude because the lighter fractions have been removed.

Producing More Light Products

The refining scheme evolved to this point is shown in Fig. 6. It is typical of a low investment refinery designed to make products of modern quality. Yet the relative amounts of products are dictated by the boiling range of the crude oil feed. For Light Arabian crude oil reported earlier (see Fig. 4), all distillate fuel oils and lighter products (those boiling below 650°F) would comprise only about 55 vol.% of the crude oil feed rate.

For industrialized areas where the principal demand is for transportation fuels or high quality heating oils, a refining scheme of the type shown in Fig. 6 would need to dispose of almost half of the crude oil as low quality, less desirable, residual products. Moreover, the price obtained for these residual products is not only much lower than revenues from lighter products but also lower than the cost of the original crude oil. Thus, there are economic incentives to convert much of the residual portions into lighter products of suitable properties.

Relative volumes of petroleum product deliveries in the United States and the portions existing in Light Arabian crude oil are compared by boiling ranges in Fig. 7. Note that 80.85 vol.% of all United States petroleum products are lighter than the boiling temperature of 650°F compared to the 55 vol.% existing in the crude oil. Furthermore, half of all United States products

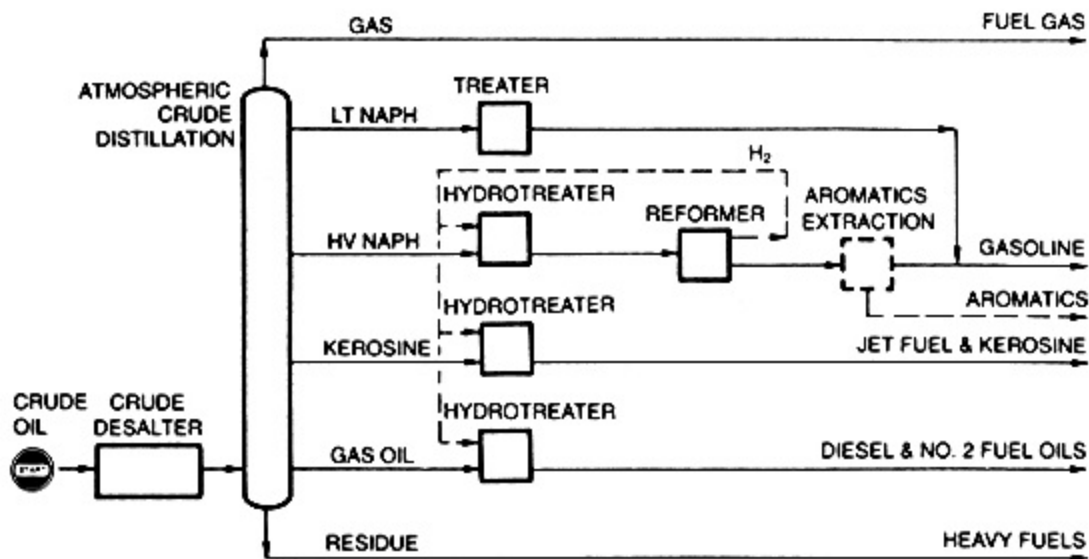


Fig. 6.

Low investment route to modern products.

are gasoline and lighter distillates (boiling temperatures less than 400°F) compared to 29 vol.% in the crude oil.

This comparison can appear unfair since an array of products obtained easily from one crude oil would be difficult to obtain from another crude oil feed. Total product deliveries in the United States come from a variety of different crude oils, processed in a variety of different refining schemes. But the comparison serves to emphasize a long term trend in the refining industry to convert heavy, less desirable fractions into lighter, more valuable products. The comparison also lays the foundation for the next group of processes to be discussed. The choice and arrangement of processes hereafter are intended to depict a breadth of refining technology, rather than suggest a commercial scheme for handling the example crude oil.

	CUT	BP, °F		PRODUCT	BP, °F
8	LT NAPH	50—200	5	GASES	-40—100
21	HV NAPH	200—400	45	GASOLINE	100—400
11	KEROSENE	400—500			
15	GAS OIL	500—650	5	JET FUEL & KEROSENE	300—500
			25	FUEL OIL	400—600
45	RESIDUE	650*	5	LUBE/ETC	600*
			15	RESIDUE	600*

Fig. 7.

Light Arabian crude oil compared to 1979 United States deliveries.

Cracking

These processes cause hydrocarbon molecules to break apart into two or more smaller molecules. Thermal cracking uses high temperature (above 650°F) and long residence time to accomplish the molecular split. Catalytic cracking accomplishes the split much faster and at lower temperatures because of the presence of a cracking catalyst.

Catalytic cracking involves not only some of the biggest units, with their large catalyst reactor-separators and regenerators, but it is also among the more profitable operations with its effective conversion of heavy feeds to light products. Gasoline from catalytic cracking has a higher octane number than thermally cracked gasoline. Yields include less gas and coke than thermal cracking; i.e., more useful liquid products are made. The distribution of products between gasoline and heating oils can be varied by different choices for catalysts and varying operating conditions.

The best feeds for catalytic crackers are determined by a number of factors. The feed should be heavy enough to justify conversion. This usually sets a lower boiling point of about 650°F. The feed should not be so heavy that it contains undue amounts of metal-bearing compounds nor carbon-forming materials. Either of these substances is more prevalent in heavier fractions and can cause the catalyst to lose activity more quickly.

Visbreaking is basically a mild, once-through thermal-cracking process. It is used to get just sufficient cracking of resid so that fuel oil specifications can be met. Although some gasoline and light distillates are made, this is not the purpose of the visbreaker.

Coking is another matter. It is a severe form of thermal cracking in which coke formation is tolerated to get additional lighter liquids from the heavier, dirtier fractions of crude oil. Here, the metals that would otherwise foul a catalytic process are laid down with the coke. The coke settles out in large coke drums that are removed from service frequently (about one a day) to have the coke cut out with high-pressure water lances. To make the process continuous, multiple coke drums are used so that some drums can be on-stream while others are being unloaded.

Hydrocracking achieves cracking with a rugged catalyst to withstand resid contaminants and with a hydrogen atmosphere to minimize coking. Hydrocracking combines hydrotreating and catalytic-cracking goals, but a hydrocracker is much more expensive than either of the other two. The pressure is so high (up to 3000 lb/in.²) that very thick walled vessels must be used for reactors (up to 9 in. thick). The products from a hydrocracker will be clean (desulfurized, denitrified, and demetalized) and will contain isomerized hydrocarbons in greater amount than in conventional catalytic cracking. A significant part of the expense of operating a hydrocracker is for the hydrogen that it consumes.

Vacuum Distillation

Among the greater variety of products made from crude oil, some of the products (lubricating oils, for example) have boiling ranges that exceed

650°F the general vicinity where cracking would occur in atmospheric distillation. Thus, by operating a second distillation unit under vacuum, the heavier parts of the crude oil can continue to be divided into specific products. Furthermore, some of the fractions distilled from vacuum units are better than atmospheric residue for cracking because the metal-bearing compounds and carbon-forming materials are more highly concentrated in the vacuum residue.

Reconstituting Gases

Cracking processes to convert heavy liquids to lighter liquids also make gases. Another way to make more liquid products is to combine gaseous hydrocarbons. A few small molecules of a gas can be combined to make one bigger molecule with fairly specific properties. Here, a gas separation unit is added to the refinery scheme to isolate the individual types of gases. When catalytic cracking is also part of the refining scheme, there will be a greater supply of olefins: ethylene, propylene, and butylene. Two routes for reconstituting these gaseous olefins into gasoline blending stocks are described below.

Polymerization ties two or more olefins together to make polymer gasoline. The double bond in only one olefin is changed to a single bond during each link between two olefins. This means the product will still have a double bond. For gasoline, these polymer stocks are good for blending because olefins tend to have higher octane numbers than their paraffin homologs.

However, the olefinic nature of polymer gasoline can also be a drawback. During long storage in warmer climates, the olefins can continue to link up to form bigger molecules of gum and sludge. This effect, though, is seldom important when the gasoline goes through ordinary distribution systems.

Alkylation combines an olefin and isobutane when gasoline is desired. The product is mostly isomers. If the olefin were butylene, the product would contain a high concentration of 2,2,4-trimethyl pentane. The reader is reminded that this is the standard compound that defines 100 on the octane number scale. Alkylates are high quality gasoline-blending compounds, having good stability as well as high octane numbers.

A Modern Refinery

A refining scheme incorporating the processes discussed so far is shown in Fig. 8. The variations are quite numerous, though. Types of crude oil available, local product demands, and competitive quality goals are just a few of the factors that are weighed to decide a specific scheme.

Many other processes play an important role in the final scheme. A partial list of these other processes would have the following goals: dewaxing lubricating oils, deoiling waxes, deasphalting heavy fractions, manufacturing specific compounds for gasoline blending (alcohols, ethers, etc.), and isolating specific fractions for use as petrochemical

feedstocks.

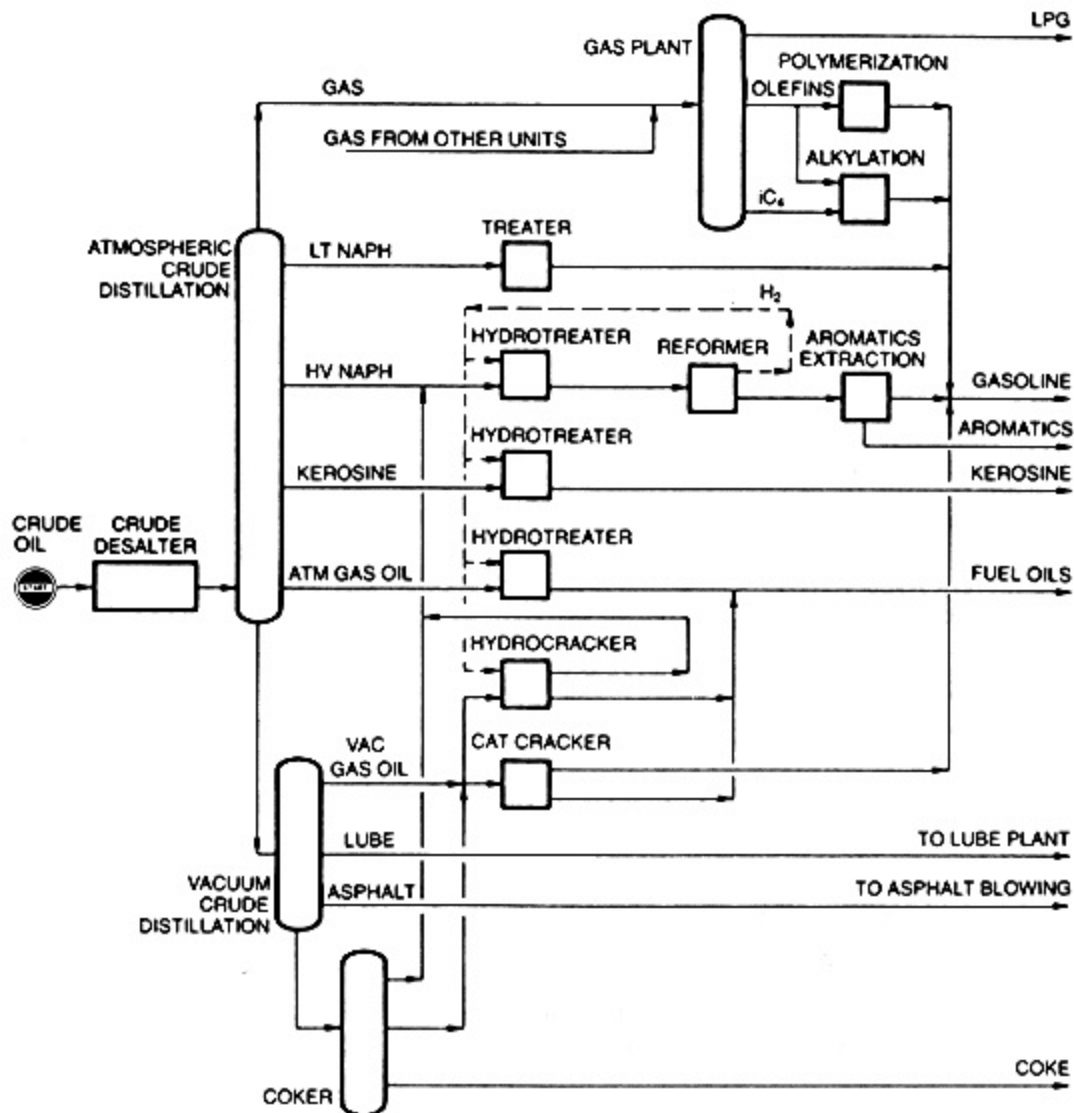


Fig. 8.
High conversion refinery.

Petrochemicals

It has already been mentioned that petrochemicals account for only a little more than 6 1/2 vol.% of all petroleum feedstocks. Earlier, Table 7 gave the vast array of the applications of these petrochemicals. Olefins and aromatics make up a big part of the total.

Ethylene is one of the most important olefins. It is usually made by cracking gasesethane, propane, butane, or a mixture of these as might exist in a refinery's off-gases. When gas feedstock is scarce or expensive, naphthas and even whole crude oil have been used in specially designed ethylene

crackers. The heavier feeds also give significant quantities of higher molecular weight olefins and aromatics.

Aromatics, as has been pointed out, are in high concentration in the product from a catalytic reformer. When aromatics are needed for petrochemical manufacture, they are extracted from the reformer's product using solvents such as glycols (the Udex process, for example) and sulfolane, to name two popular ones.

The mixed aromatics are called BTX as an abbreviation for benzene, toluene, and xylene. The first two are isolated by distillation and the isomers of the third are separated by partial crystallization. Benzene is the starting material for styrene, phenol, and a number of fibers and plastics. Toluene is used to make a number of chemicals, but most of it is blended into gasoline. Xylene use depends on the isomer, p-xylene going into polyester and o-xylene going into phthalic anhydride. Both are involved in a wide variety of consumer products.

Process Details

So far, refining units have been described as they relate to other units and to final product specifications. Now, typical flow diagrams of some major processes will be presented to highlight individual features. In many cases the specific design shown herein is an arbitrary choice from among several equally qualified designers.

Crude Desalting

Basically a water-washing process, the crude desalter must accomplish intimate mixing between the crude oil and water, then separate them sufficiently so that water will not enter subsequent crude-oil distillation heaters.

A typical flow diagram is shown in Fig. 9. The unrefined crude oil is heated to 100-300°F for suitable fluid properties. The operating pressure is 40 lb/in.² gauge or more. Elevated temperatures reduce oil viscosity for better mixing, and elevated pressure suppresses vaporization. The washwater can be added either before or after heating.

Mixing between the water and crude oil is assured by passing the mixture through a throttling valve or emulsifier orifice. Trace quantities of caustic, acid, or other chemicals are sometimes added to promote treating. Then the water-in-oil emulsion is introduced into a high voltage electrostatic field inside a gravity settler. The electrostatic field helps the water droplets to agglomerate for easier settling.

Salts, minerals, and other water-soluble impurities in the crude oil are carried off with the water discharged from the settler. Clean desalted crude oil flows from the top of the settler and is ready for subsequent refining.

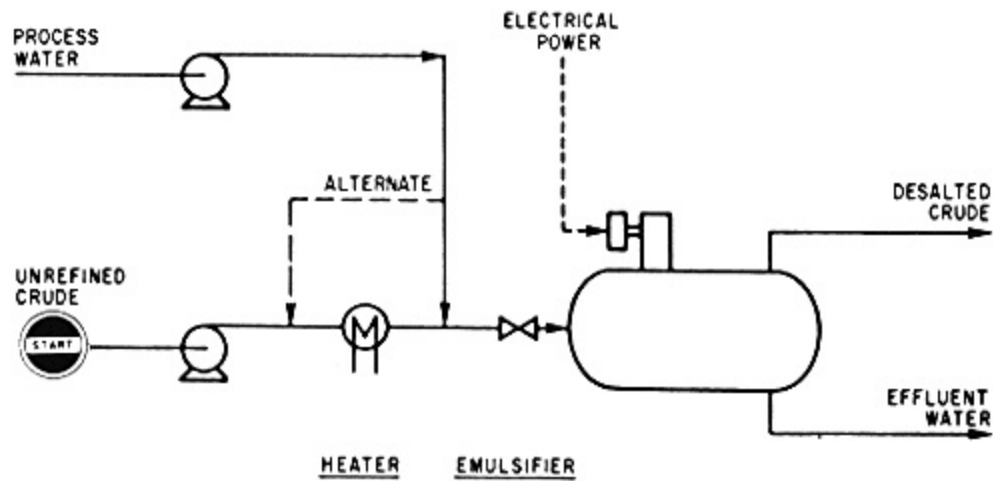


Fig. 9.
Crude desalting.
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Additional stages can be used in series to get additional reduction in salt content of the crude oil. Two stages are typical, but some installations use three stages. The increased investment cost for multiple stages is offset by reduced corrosion, plugging, and catalyst poisoning in downstream equipment by virtue of lower salt content.

Crude Distillation

Single or multiple distillation columns are used to separate crude oil into fractions determined by their boiling range. Common identification of these fractions was discussed in connection with Fig. 5, but these should only be considered as a guide since a variety of refining schemes call for altering the type of separation made at this point.

A typical flow diagram of a three-stage crude distillation system [14] is shown in Fig. 10. The crude oil is heated by exchange with various hot products coming from the system before it passes through a fired heater. The temperature of the crude oil entering the first column is 600-700°F, or high enough to vaporize the heavy gas oil and all lighter fractions. The first column is depicted as having a larger diameter in the lower section because the quantity of vapors and liquids passing through this section require more cross-sectional area to avoid high pressure drop across individual contacting trays or to prevent high-velocity vapors from blowing the liquid up the column rather than giving good mixing as the liquids follow their normal path down the column. The final design depends upon the quantities of individual fractions and permitted tower loadings.

Since light products must pass from the feed point up to their respective drawoff point, any intermediate stream will contain some of these lighter materials. Stream stripping (note the group of steam strippers beside the first

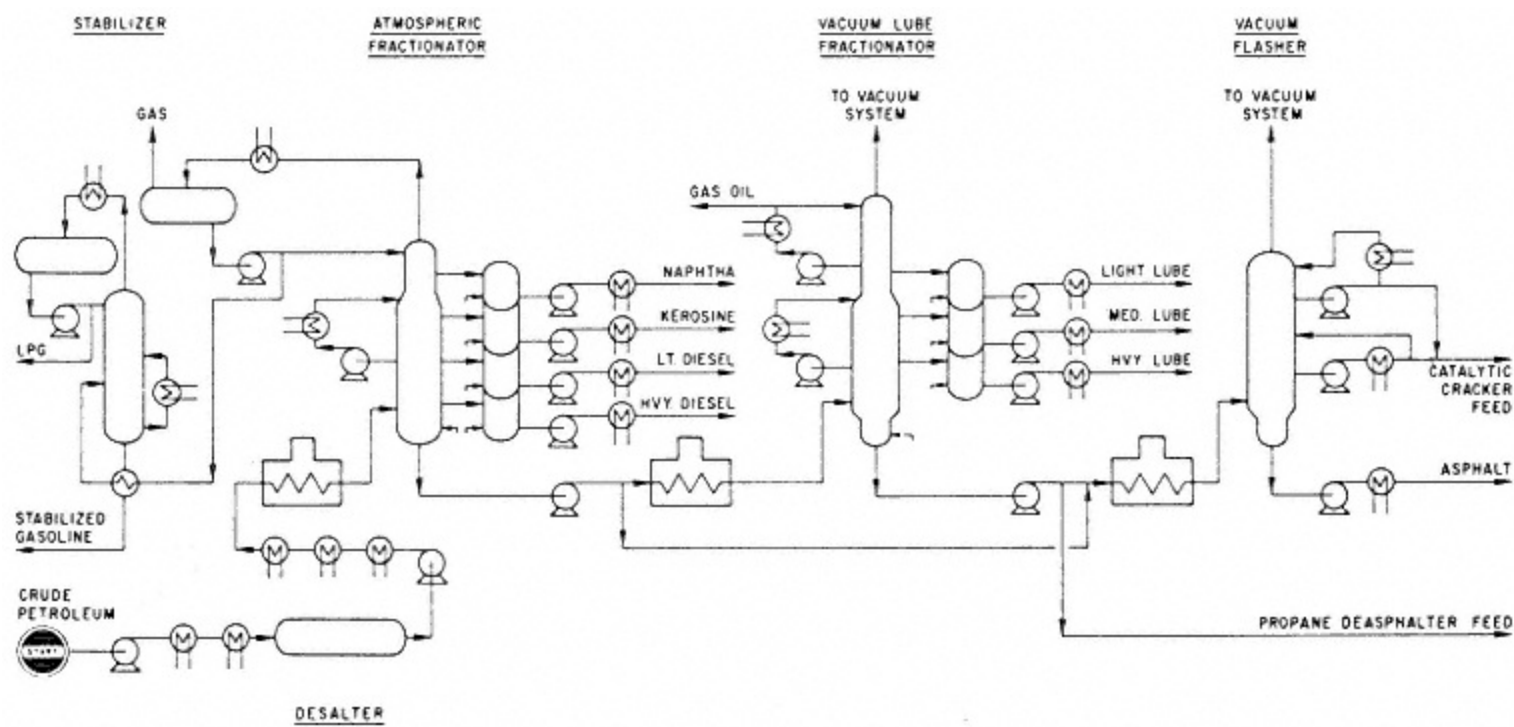


Fig. 10.
Crude distillationFoster Wheeler Corp.
(Reprinted from Ref. 14 with permission.)

column in Fig. 10) is a way to reintroduce these light materials back into the tower to continue their passage up through the column.

The next two fractionating columns of Fig. 10 are operated under vacuum. Steam jet ejectors are used to create the vacuum so that the absolute pressure can be as low as 3040 mmHg. The vacuum permits hydrocarbons to be vaporized at temperatures much below their normal boiling points. Thus, fractions with boiling points above 650°F can be separated with vacuum distillation without causing thermal cracking. Steam is often added to vacuum units to reduce the partial pressure of the hydrocarbons even further. If the steam is added ahead of the furnace associated with the vacuum columns, fluid velocity through the furnace tubes is increased and coke formation is minimized.

Lately, a popular addition to a crude distillation system has been a preflash column ahead of the two stages shown in Fig. 10. The preflash tower strips out the lighter portions of a crude oil before the remainder enters the atmospheric column. It is the lighter portions that set the vapor loading in the atmospheric column which, in turn, determines the diameter of the upper section of the column.

Incidentally, total refining capacity of a facility is reported in terms of its crude-oil handling capacity. Thus, the size of the first distillation column, whether a preflash or an atmospheric distillation column, sets the reported size of the entire refinery. Ratings in barrels per stream day (BPSD) will be greater than barrels per calendar day (BPCD). Processing units must be shut down on occasion for maintenance, repairs, and equipment replacement. The ratio of operating days to total days (or BPCD divided by BPSD) is called an "on-stream factor" or "operating factor." The ratio will be expressed either as a percent or a decimal. For example, if a refinery unit undergoes one shutdown period of one month during a three year duration, its operating factor is $(36 - 1)/36$, or 0.972, or 97.2%.

Outside the United States, refining capacity is normally given in metric tons per year. Precise conversion from one unit of measure to the other depends upon the specific gravity of the crude oil, but the approximate relation is one barrel per day equals 50 tons per year.

Hydrotreating

This is a catalytic hydrogenation process that reduces the concentration of sulfur, nitrogen, oxygen, metals, and other contaminants in a hydrocarbon feed. In more severe forms, hydrotreating saturates olefins and aromatics.

A typical flow diagram is shown in Fig. 11. The feed is pumped to operating pressure and mixed with a hydrogen-rich gas, either before or after being heated to the proper reactor inlet temperature. The heated mixture passes through a fixed bed of catalyst where exothermic hydrogenation reactions occur. The effluent from the reactor is then cooled and sent through two separation stages. In the first, the high-pressure separator,

unreacted hydrogen is taken overhead to be scrubbed for hydrogen sulfide removal; the cleaned hydrogen is then recycled. In the second, the lower-pressure separator

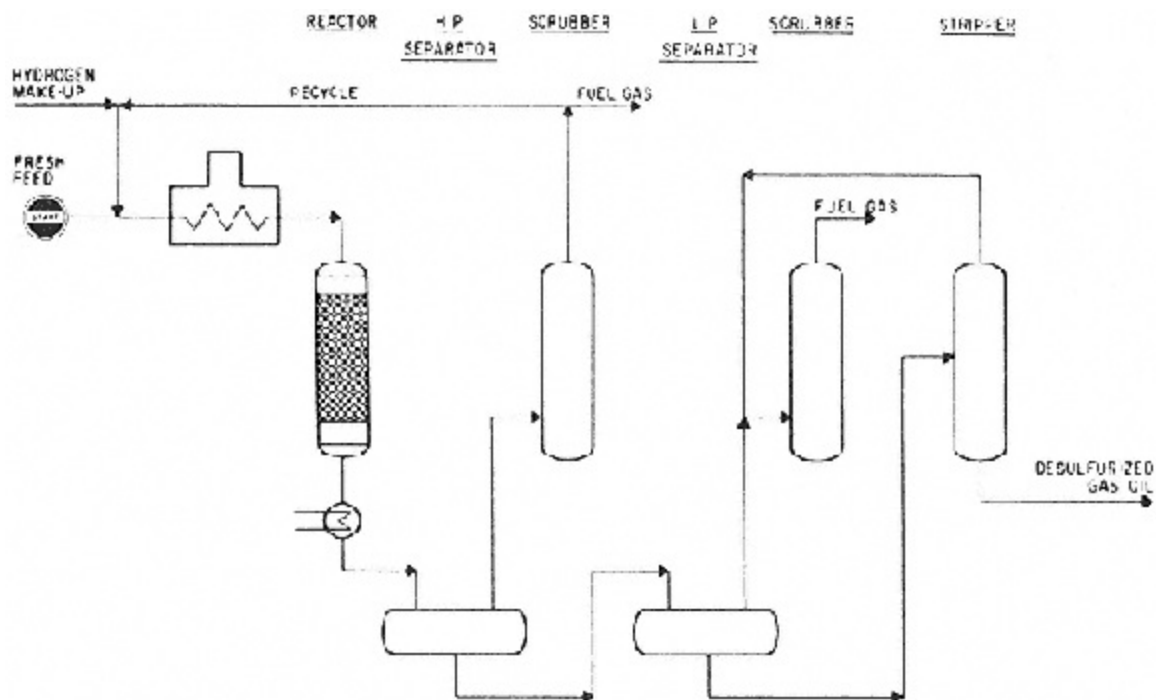


Fig. 11.

Gulfingulf R&D Co. and Houdry Division of Air Products and Chemicals, Inc.
(Reprinted from Ref. 10 with permission.)

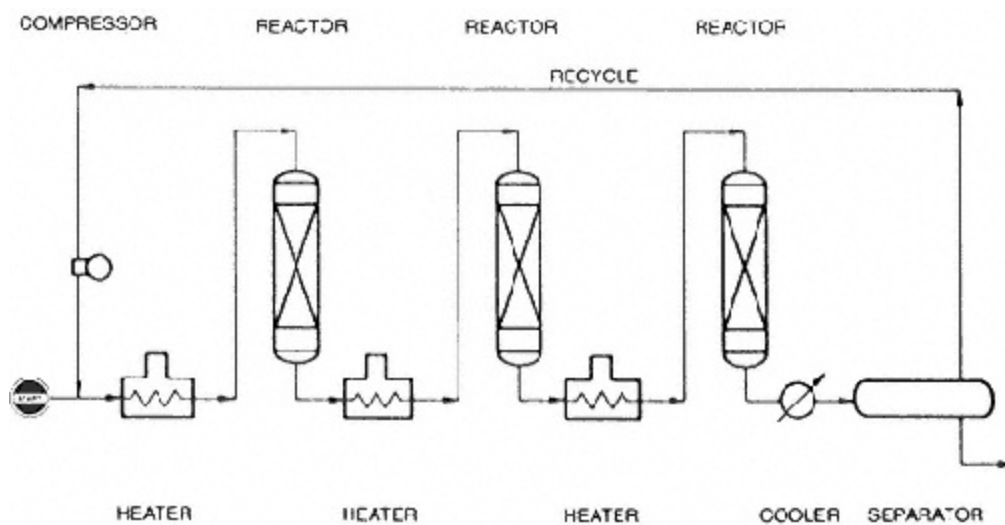


Fig. 12.

Catalytic reforming, generalized flow diagram.

takes off the remaining gases and light hydrocarbons from the liquid product. If the feed is a wide-boiling range material from which several blending stocks are to be made, the second separator can be a distillation column for removing gases and light hydrocarbons, with sidestreams used for each of the liquid products.

The feed for hydrotreating can be a variety of different boiling range materials extending from light naphtha to vacuum residues. Generally, each fraction is treated separately to permit optimum conditions the higher boiling materials requiring more severe treating conditions. For example, naphtha hydrotreating can be carried out at 200–500 lb/in.² abs and at 500–650°F, with a hydrogen consumption of 10–50 SCF/bbl of feed. On the other hand, a residue hydrotreating process can operate at 1000–2000 lb/in.² abs and at 650–800°F, with a hydrogen consumption of 600–1200 SCF/bbl [13]. Nevertheless, hydrotreating is such a desirable clean-up step that it can justify its own hydrogen manufacturing facilities, although the hydrogen-rich stream obtained as a by-product from catalytic reforming usually is sufficient for most operations.

Catalyst formulations constitute a significant difference among hydrotreating processes. Each catalyst is designed to be better suited to one type of feed or one type of treating goal [15]. When hydrotreating is done for sulfur removal, the process is called hydrodesulfurization and the catalyst generally is cobalt and molybdenum oxides on alumina. A catalyst of nickel-molybdenum compounds on alumina can be used for denitrogenation and cracked stock saturation.

Catalytic Reforming

Some confusion comes from the literature when the term "naphtha reforming" is used to designate processes to make synthesis gas a mixture containing predominantly carbon monoxide and hydrogen. However, naphtha reforming has another meaning and is the one intended here production of an aromatic-rich liquid for use in gasoline blending.

A typical flow diagram is shown in Fig. 12. The feed is pumped to operating pressure and mixed with a hydrogen-rich gas before heating to reaction temperatures. Actually, hydrogen is a by-product of the dehydrogenation and cyclization reactions, but by sustaining a hydrogen atmosphere, cracking and coke formation are minimized.

The feed for catalytic reforming is mostly in the boiling range of gasoline to start with. The intent is to convert the paraffin and naphthene portions to aromatics. As an example, a 180–310°F fraction of Light Arabian crude oil was reported to have 8 vol.% aromatics before catalytic reforming, but was 68 vol.% aromatics afterwards. The feed paraffin content (69 vol.%) was reduced to less than half, and the feed naphthene content (23 vol.%) was almost completely absent in the product [16].

The extent of octane number change with changes in molecular configuration is shown in Table 8 where normal paraffins and naphthenes are compared with their aromatic homologs.

TABLE 8 Aromatics Have Higher Octane Numbers [6]

Hydrocarbon Homologs		Octane Number, Clear	
		Motor	Research
C7 hydrocarbons			
n-Paraffin	C7H16 (n-heptane)	0.0	0.0
Naphthene	C7H14 (cycloheptane)	40.2	38.8
	C7H14 (methylcyclohexane)	71.1	74.8
Aromatic	C7H8 (toluene)	103.5	120.1
C8 hydrocarbons:			
n-Paraffin	C8H18 (n-octane)	-15a	-19a
Naphthene	C8H16 (cyclooctane)	58.2	71.0
	C8H16 (ethylcyclohexane)	40.8	45.6
Aromatic	C8H10 (ethylbenzene)	97.9	107.4
	C8H10 (o-xylene)	100.0	120a
	C8H10 (m-xylene)	115.0	117.5
	C8H10 (p-xylene)	109.6	116.4

aBlending value at 20 vol.% in 60 octane number reference fuel.

If the naphthenes are condensed (multirings or indanes), they tend to deactivate the reforming catalyst quickly. Control of the end point of the feed will exclude these deactivating compounds.

Catalysts which promote reforming reactions can give side-reactions. Isomerization is acceptable but hydrocracking gives unwanted saturates and gases. Therefore, higher operating pressures are used to suppress hydrocracking. This remedy has disadvantages. Higher pressures suppress reforming reactions too, although to a lesser extent. Generally, a compromise is made between desired reforming and undesired hydrocracking. The effects of operating conditions on competing reactions [17] are shown in Table 9.

In the late 1960s it was discovered that the addition of certain promoters, such as rhenium, germanium, or tin, to the platinum-containing catalyst would reduce cracking and coke formation. The resulting catalysts are

TABLE 9 Favored Operating Conditions for Desired Reaction Rates [17]

Feed	Reaction	Product	Desired Rate	To Get Desired Rate	
				Pressure	Temperature
Paraffins	Isomerization	Isoparaffins	Increase	Increase	Increase
	Dehydrocyclization	Naphthenes	Increase	Decrease	Increase
	Hydrocracking	Lower molecular weight	Decrease	Decrease	Decrease
Naphthenes	Dehydrogenation	Aromatics	Increase	Decrease	Increase
	Isomerization	Isoparaffins	Increase	Increase	Increase
	Hydrocracking	Lower molecular weight	Decrease	Decrease	Increase
Aromatics	Hydrodealkylation	Lower molecular weight	Decrease	Decrease	Decrease

referred to as bimetallic catalysts. These newer catalysts permit the process to enjoy the better reforming conditions of lower pressure without being unduly penalized by hydrocracking. Earlier pressures of 500 lb/in.² gauge are now down to 150 lb/in.² gauge.

Operating temperatures are important, too. The reactions are endothermic. Best yields would come from isothermal reaction zones, but this is difficult to achieve. Instead, the reaction beds are separated into a number of adiabatic zones operating at 500-1000°F with heaters between stages to supply the necessary heat of reaction and hold the overall train near a constant temperature. Three or four reactor zones are commonly used when it is desired to have a product with high octane numbers.

In the recent push to make gasoline with high octane numbers but without the use of antiknock additives, high severity catalytic reforming is the prime route. The big disadvantage is a yield loss. Newer catalysts make the loss less dramatic, but the penalty remains [18], as can be seen from Fig. 13.

Catalytic Cracking

A typical diagram of a fluid catalytic cracker is shown in Fig. 14. The unit is characterized by two huge vessels, one to react the feed with hot catalyst and the other to regenerate the spent catalyst by burning off carbon with air. The activity of the newer molecular-sieve catalysts is so great that the contact time

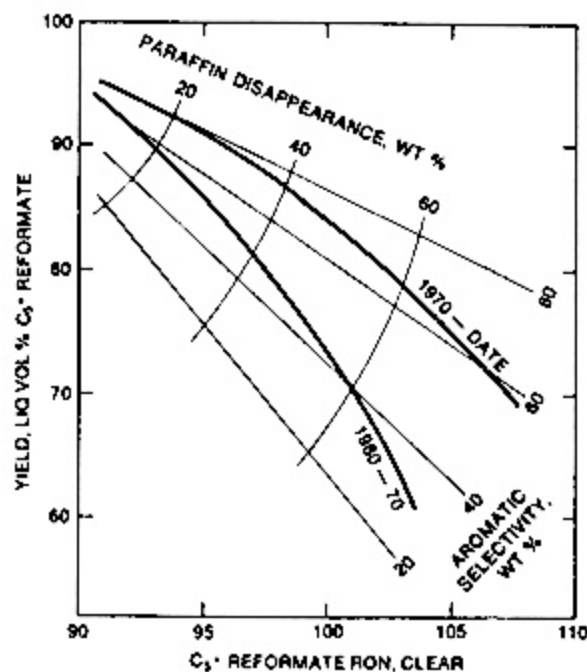


Fig. 13.
Better octane numbers, less yield (Kuwait naphtha).
(Reprinted from Ref. 18 with permission.)

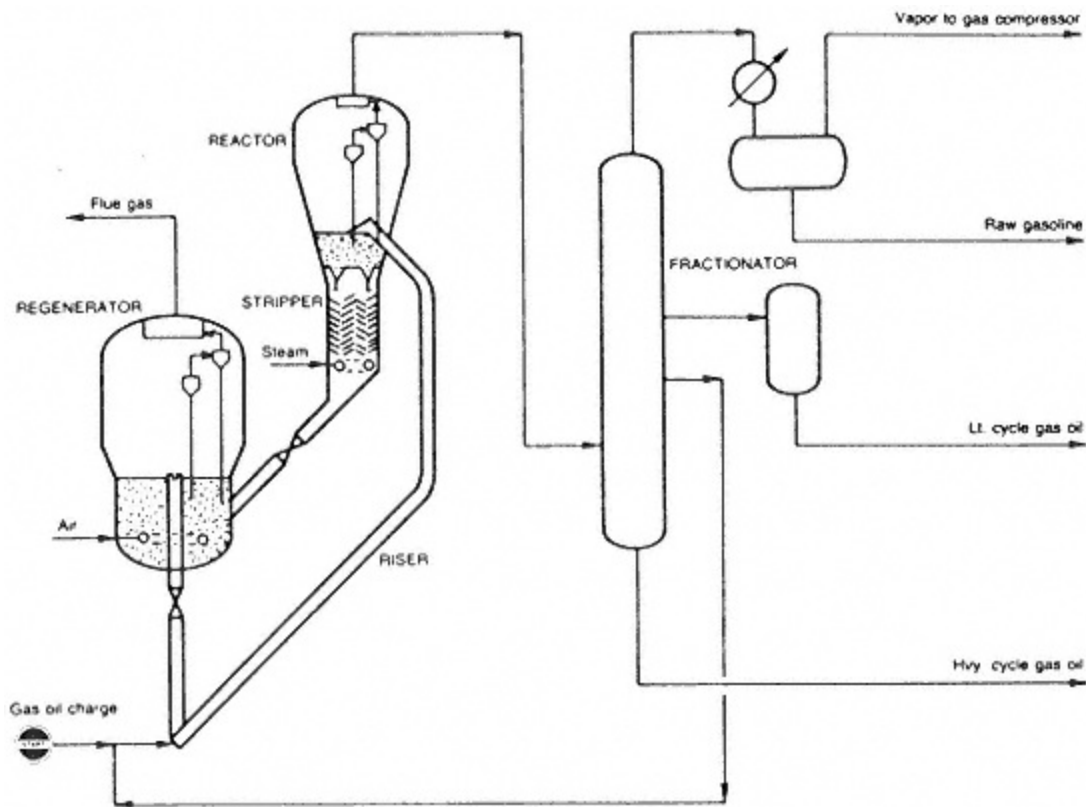


Fig. 14.

Fluid catalytic cracking Texaco Development Corp.
(Reprinted from Ref. 10 with permission.)

between feed and catalyst is reduced drastically. If not, the oil will overcrack to give unwanted gases and coke. The short contact time is accomplished using a transfer line between the regenerator and reactor vessels. In fact, the major portion of the reaction occurs in this piece of pipe or riser and the products are taken quickly overhead. The main reactor vessels then are used to hold cyclone separators to remove the catalyst from the vapor products and to give additional space for cracking the heavier portions of the feed.

There are several configurations of reactors and regenerators. In some designs, one vessel is stacked on top of the other. All are big structures (150-200 ft high).

Riser cracking, as the short-time contacting is called, has a number of advantages. It is easier to design and operate. It can be operated at higher temperatures to give more gasoline olefins. It minimizes the destruction of any aromatics formed during cracking. The net effect can be the production of gasoline having octane numbers 2 or 3 numbers higher than earlier designs would give.

Better regeneration of the spent catalyst is obtained by operating at higher temperatures (1300-1400°F) [19]. The coke that is deposited on the catalyst is

more completely burned away by higher temperature air blowing. The newer catalysts are rugged enough to withstand the extra heat, and newer metallurgy gives the regenerator vessel the strength it needs at higher temperatures.

Heavier feedstocks can be put into catalytic crackers. The nickel, vanadium, and iron in these heavier fractions do not deactivate the catalysts as fast as they once did because passivators are available now to add to the catalysts [20]. The extra sulfur that comes with heavier feeds can be prevented from exhausting into the atmosphere during regeneration because of catalysts that hold on to the sulfur compounds until the catalysts get into the reactor [21]. Then the sulfur compounds are cracked to light gases and leave the unit with the cracked products. Ordinary gas treating methods are used to capture the hydrogen sulfide coming from the sulfur in the feedstock.

Coking

Coking is an extreme form of thermal cracking. The process converts residual materials that might not easily be converted by the more popular catalytic cracking process. Coking is also a less expensive process for getting more light stocks from residual fractions. In the coking process, the coke is considered a by-product that is tolerated in the interest of more complete conversion of residues to lighter liquids.

A typical flow diagram of a delayed coker is shown in Fig. 15. There are several possible configurations, but in this one the feed goes directly into the product fractionator in order to pick up heavier products to be recycled to the cracking operation. The term "delayed coker" signifies that the heat of cracking is added by the furnace and the cracking occurs during the longer residence time in the following coke drums. Furnace outlet temperatures are in the range of 900 to 950°F while the coke drum pressures are in the range of 20 to 60 lb/in.² gauge.

The coke accumulates in the coke drum and the remaining products go overhead as vapors to be fractionated into various products. In this case, the products are gas, naphtha, light gas oil, heavy gas oil, and coke. When a coke drum is to be emptied, a large drilling structure mounted on top of the drum is used to make a center hole in the coke formation. The drill is equipped with high-pressure water jets (3000 lb/in.² gauge or more) to cut the coke from the drum so that it can fall out a bottom hatch into a coke pit. From there, belt conveyors and bucket cranes move the coke to storage or to market [22].

Fluid Coking is a proprietary name given to a different type of coking process in which the coke is suspended as particles in fluids flowing from a reactor to a heater and back again. When part of the coke is gasified, the process is called Flexicoking. Both Fluid Coking and Flexicoking are proprietary processes of Exxon Research and Engineering Co.

A flow diagram for Flexicoking is shown in Fig. 16. The first two vessels are typical of Fluid Coking in which part of the coke is burned in the heater in order to have hot coke

nuclei to contact the feed in the reactor vessel. The cracked products are quenched in an overhead scrubber where entrained coke is returned to the reactor. Coke from the reactor circulates to the heater

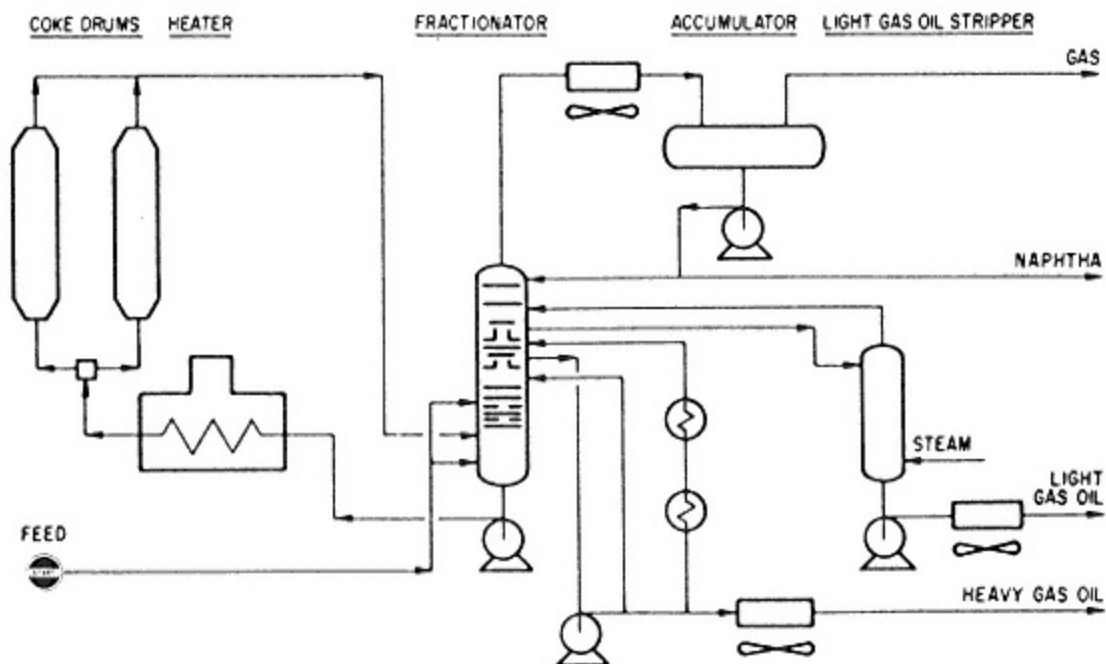


Fig. 15.
Delayed cokingFoster Wheeler Energy Corp.
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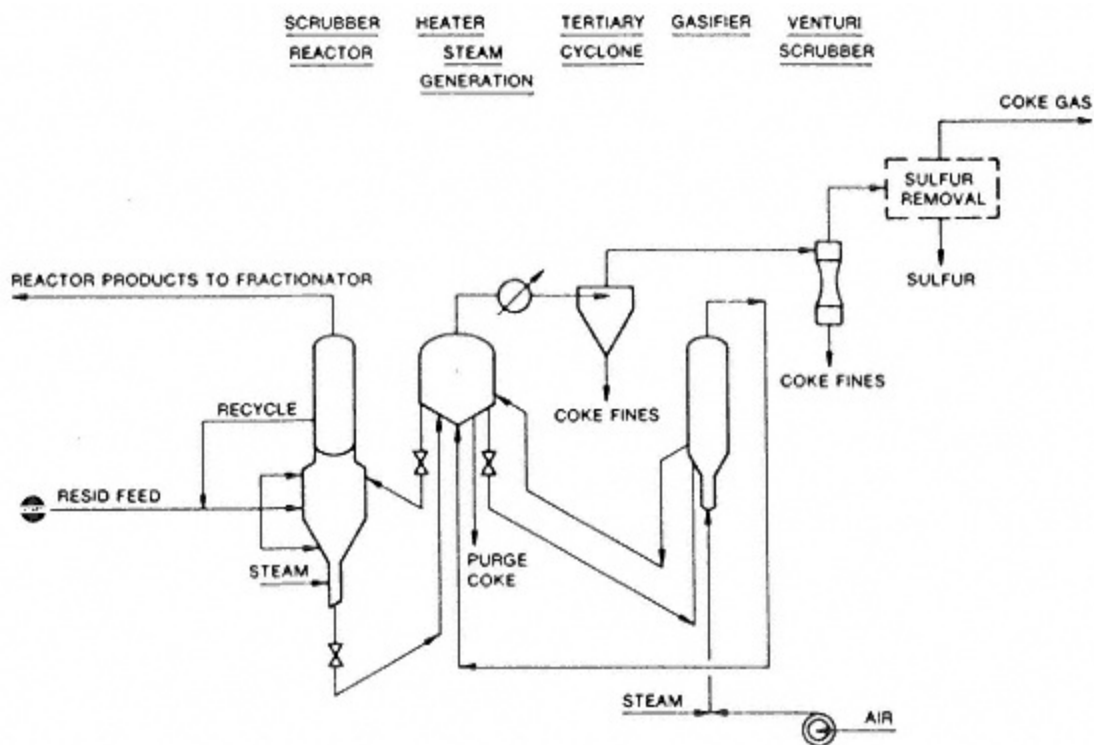


Fig. 16.
FlexicokingExxon Research and Engineering Co.
(Reprinted from Ref. 10 with permission.)

where it is devolatilized to yield a light hydrocarbon gas and residual coke. A sidestream of coke is circulated to the gasifier where, for most feedstocks, 95% or more of the gross coke product from the reactor is gasified at elevated temperature with steam and air. Sulfur that enters the unit with the feedstock eventually becomes hydrogen sulfide exiting the gasifier and is recovered by a sulfur removal step.

Hydrocracking

Before the late 1960s, most hydrogen used in processing crude oil was for pretreating catalytic reformer feed naphtha and for desulfurizing middle-distillate products. Soon thereafter, requirements to lower sulfur content in most fuels became an important consideration. The heavier fractions of crude oil were the hardest to treat. Moreover, these fractions were the ones offering additional sources of light products. This situation set the stage for the introduction of hydrocracking.

A typical flow diagram for hydrocracking is shown in Fig. 17. Process flow is similar to hydrotreating in that feed is pumped to operating pressure, mixed with a hydrogen-rich gas, heated, passed through a catalytic reactor, and distributed among various fractions. Yet the hydrocracking process is unlike hydrotreating in several important ways. Operating pressures are very high, 2000-3000 lb/in.² gauge. Hydrogen consumption also is high, 1200-1600 SCF of hydrogen per barrel of feed depending on the extent of the cracking [13]. In fact, it is not uncommon to see hydrocrackers built with their own hydrogen manufacturing facilities nearby.

The catalysts for hydrocracking have a dual function. They give both hydrogenation and dehydrogenation reactions and have a highly acidic support to foster cracking. The hydrogenation-dehydrogenation component of the catalysts are metals such as cobalt, nickel, tungsten, vanadium,

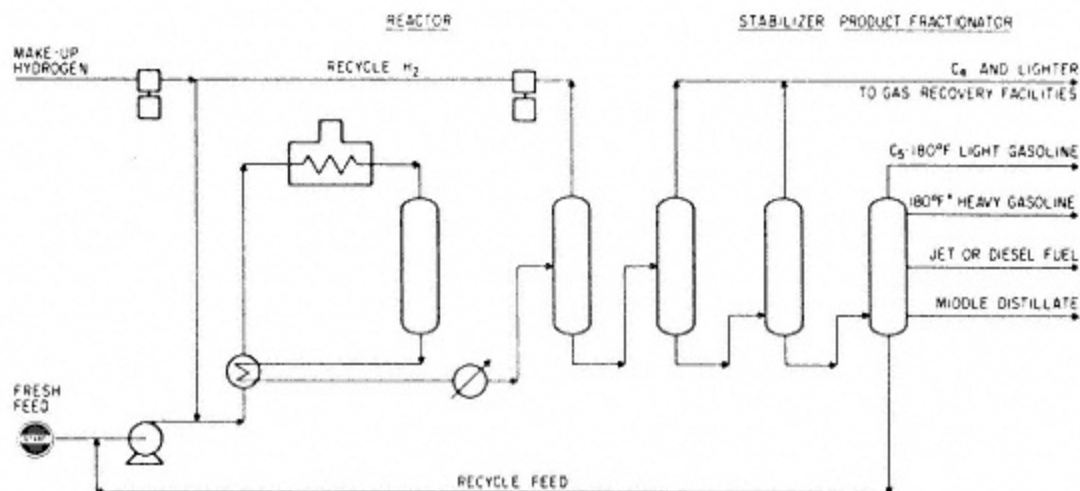


Fig. 17.
IsocrackingChevron Research Co.
(Reprinted from Ref. 10 with permission.)

molybdenum, platinum, palladium, or a combination of these metals. The acidic support can be silica-alumina, silica-zirconia, silica-magnesia, alumina-boria, silica-titania, acid-treated clays, acidic-metal phosphates, or alumina, to name some given in the literature [23].

Great flexibility is attributed to most hydrocracking processes. Under mild conditions the process can function as a hydrotreater. Under more severe conditions of cracking, the process produces a varying ratio of motor fuels and middle distillates, depending on the feedstock and operating variables. Even greater flexibility is possible for the process during design stages when it can be tailored to change naphthas into liquefied petroleum gases or convert heavy residues into lighter products.

Because the hydrocracker is viewed as both a cracker and a treater, it can appear in refining process schemes in a number of different places. As a cracker, it is used to convert feeds that are too heavy or too contaminant-laden to go to catalytic cracking. As a treater, it is used to handle heating-oil fractions that need to be saturated to give good burning quality. But it is the trend to heavier feeds and lighter high-quality fuels that causes hydrocracking to offer advantages to future refining, even though the hydrocracking units are much more expensive to build and to operate.

The principle of an ebulliating catalyst bed is embodied in some proprietary designs, in contrast with the fixed-catalyst beds used in other versions of hydrocracking. The H-Oil process of Hydrocarbon Research, Inc. and the LC-Fining process jointly licensed by C-E Lummus and Cities Service Research and Development Co. are examples of hydrocracking processes that use a mixed-reaction bed instead of a fixed bed of catalyst.

Polymerization

This process usually is associated with the manufacture of plastic films and fibers from light hydrocarbon olefins with products like polyethylene and polypropylene. As a gasoline manufacturing process, the polymerization of light olefins emphasizes a combination of only two or three molecules so that the resulting liquid will be in the gasoline boiling range.

For early polymerization units the catalyst was phosphoric acid on a quartz or kieselguhr support. Many of these units were shut down when the demand for gasoline with increased octane numbers prompted the diversion of the olefin feeds to alkylation units that gave higher octane number products. Yet some refinery balances have more propylene than alkylation can handle, so a newer version of polymerization was introduced [24]. It is the Dimersol process of the Institut Français du Pétrole for which the flow diagram is shown in Fig. 18.

The Dimersol process uses a soluble catalytic complex injected into the feed before it enters the reactor. The heat of reaction is taken away by circulating a portion of the bottoms back to the reactor after passing through a cooling water exchanger. The

product goes through a neutralizing system that uses caustic to destroy the catalyst so that the resulting polymer is clean and stable. Typical octane number ratings for the product are 81 Motor and 96.5 Research, unleaded.

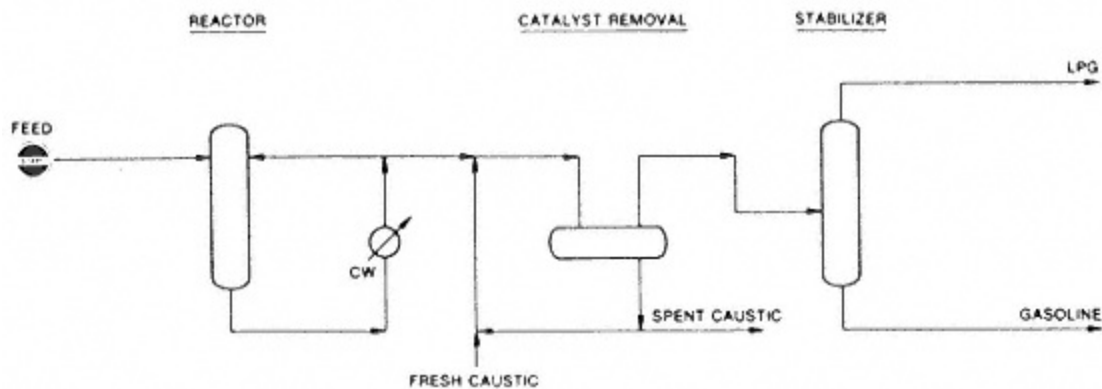


Fig. 18.
Dimersol Institut Francais du Petrole.
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Alkylation (See Articles on Alkylation)

This is another process that increases the total yield of gasoline by combining some of the gaseous light hydrocarbons to form bigger molecules boiling in the gasoline range. Alkylation combines isobutane with a light olefin, typically propylene and butylene. A flow diagram for an alkylation unit using hydrofluoric acid as a catalyst is shown in Fig. 19.

Common catalysts for gasoline alkylation are hydrofluoric acid or sulfuric acid. The reaction is favored by higher temperatures, but competing reactions among the olefins to give polymers prevent high quality yields. Thus, alkylation usually is carried out at low temperatures in order to make the alkylation reaction predominate over the polymerization reactions. Temperatures for hydrofluoric acid catalyzed reactions are approximately 100°F and for sulfuric acid they are approximately 50°F. Since the sulfuric-acid catalyzed reactions are carried out at below normal atmospheric temperatures, refrigeration facilities are included.

Alkylate product has a high concentration of 2,2,4-trimethyl pentane, the standard for the 100 rating of the octane number scale. Other compounds in the alkylate are higher or lower in octane number, but the lower octane number materials predominate so that alkylate has a Research octane number in the range of 92 to 99. Developments are underway to slant the reactions in favor of the higher octane materials [25]. Random samples of alkylate quality reported in the literature [26] are summarized in Table 10.

TABLE 10 Typical Alkylate Octane Numbers [25]

	Feed Olefin			
	C2	C3	C3+C4	C4
Research octane number, clear	101.5	90.5	93	96.5
Motor octane number, clear	93	89	91	95.5

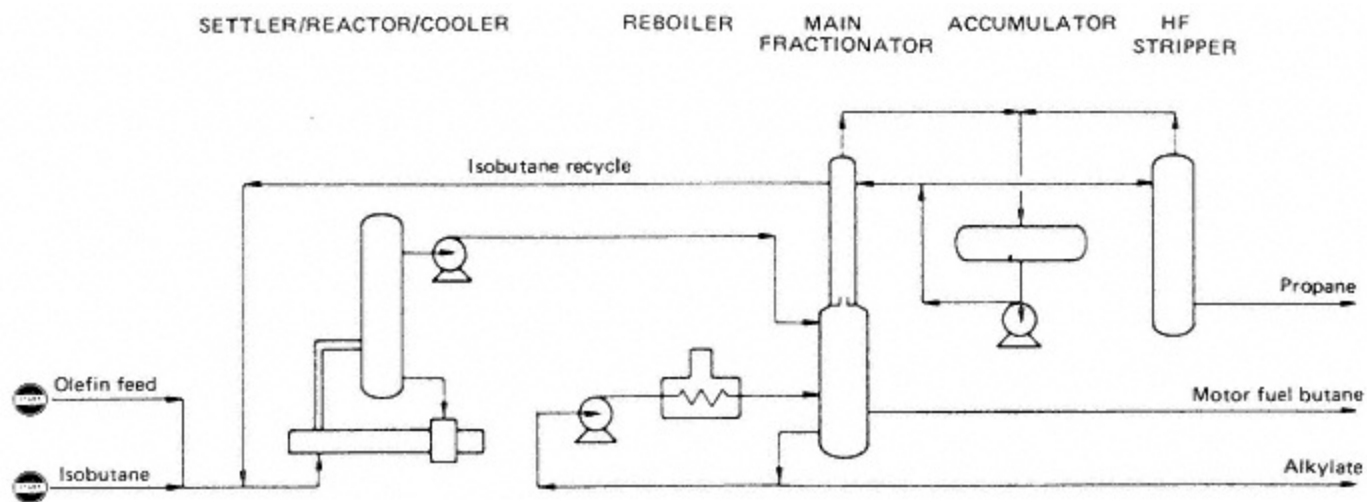


Fig. 19.
HF alkylation Phillips Petroleum Co.
(Reprinted from Ref. 10 with permission.)

Ethylene

The evolution of cracking to make ethylene has progressed along two lines. In one, the ethylene is a by-product of fuel manufacturing, with the feedstock sometimes being a less desirable fuel material and at other times being a heart cut from some very desirable fuel material like naphtha. In the other line of progression, ethylene is pursued as a growing business of its own, with heavier by-product liquids being treated for use as gasoline blending stocks.

A popular starting material for ethylene cracking is ethane or propane. Some forecasts [27] suggest that these light hydrocarbon feeds may not be available in the growing volumes needed to keep up with a predicted 4.55% per year growth in ethylene demand. Thus many recent ethylene-cracking processes are tailored to handle heavier feedstocks. A flow diagram of an ethylene cracker [28] is shown in Fig. 20.

The feedstock is preheated and mixed with steam to be cracked in a tubular pyrolysis furnace. The products leave the furnace at 1400-1600°F and are rapidly quenched in an exchanger and sent to a gasoline fractionator where heavy fractions are removed. The gaseous products go to a quench

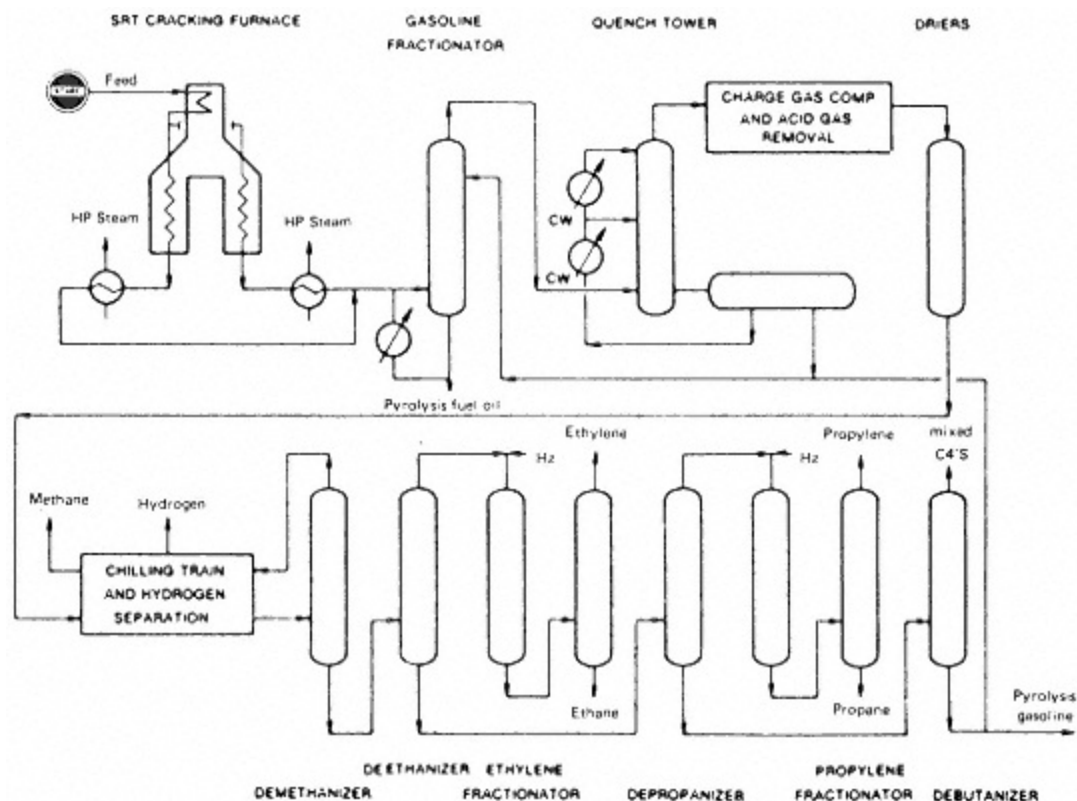


Fig. 20.
EthyleneC-E Lummus.
(Reprinted from Ref. 28 with permission.)

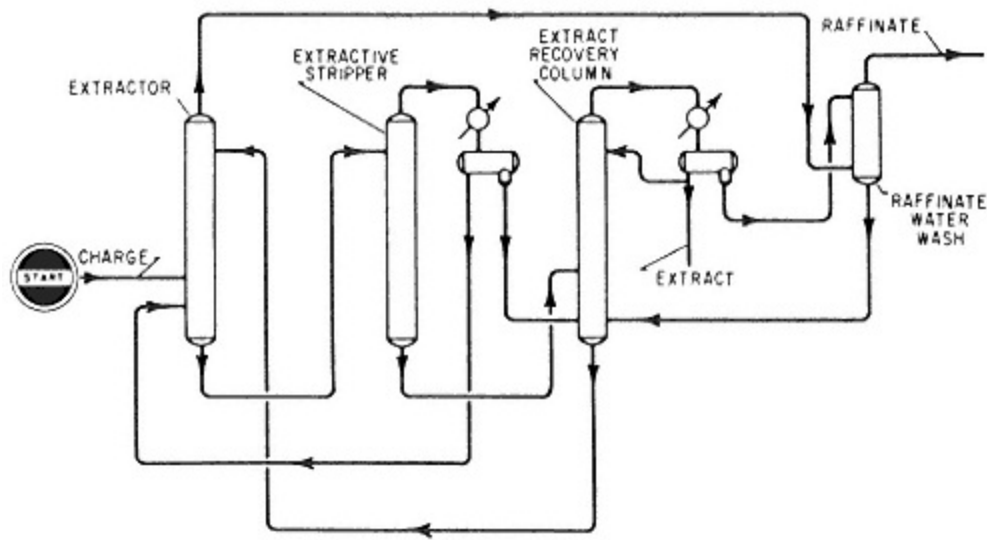


Fig. 21.

Sulfone extraction UOP Process Division of UOP, Inc., for process originally developed by Royal Dutch/Shell group.
(Reprinted from Ref. 10 with permission.)

tower where direct water quench stops any further reaction. The flow diagram shows that the remainder of the process is intended to get light gas separation of the product.

The main derivatives of ethylene are polyvinyl chloride (PVC), ethylene glycol, and polyethylene.

Aromatics

Benzene, toluene, xylene, and ethylbenzene are made mostly from catalytic reforming of naphthas with units like those already discussed. As a gross mixture, these aromatics are the backbone of gasoline blending for high octane numbers. However, there are many chemicals derived from these same aromatics [29]. Thus many aromatic petrochemicals have their beginning by selective extraction from naphtha or gas-oil reformate.

A typical extraction process is the Sulfolane extraction process [10] shown in Fig. 21. The reformate is fed to a contactor for the countercurrent extraction of aromatic components with sulfolane solvent. The solvent, rich in aromatics, goes to a stripper and recovery column where the aromatics are separated from the solvent. Aromatic recoveries and purities are varied by choosing suitable operating parameters.

Refinery Size and Cost

The few, truly huge refineries give the impression that most refineries are big. The bigger world refineries have a capacity of more than 600,000. BPD [30]. Yet one should not be misled by a so-called "average" refinery designed for

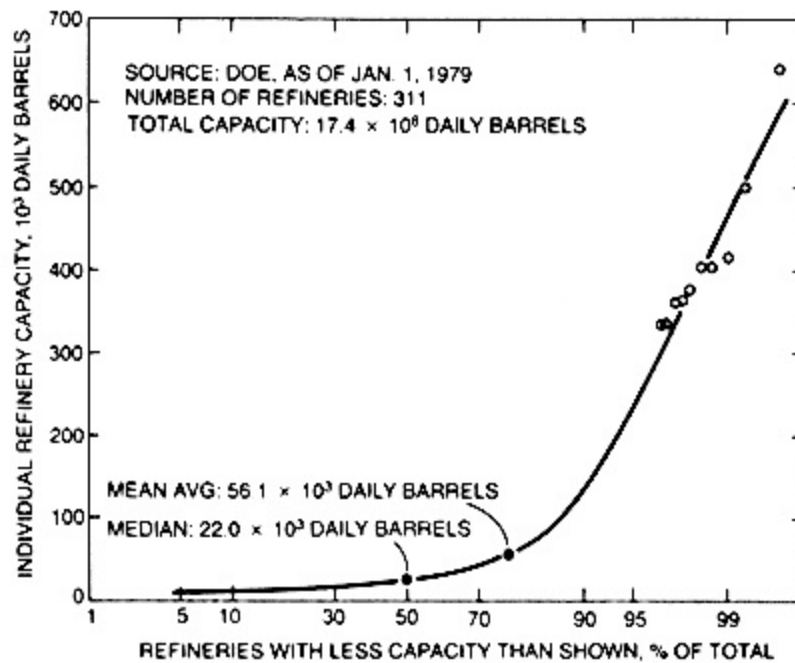


Fig. 22.

United States refinery size distribution as of January 1, 1979.

100,000 BPD. Actually, the mean average size of the 240 refineries in the United States operating as of the first of 1988 was 58,250 BPD, computed from U.S. Department of Energy data [31]. Moreover, half of these refineries are only about 22,000 BPD (the median) or less. A distribution plot for United States refinery sizes is shown in Fig. 22 (as of 1980).

TABLE 11 Distribution of Unit Costs

Process Unit	Relative Capacity (vol.%)	Unit ^b Cost (\$/BPD)	Cost as Part of Total Refinery ^b (\$/BPD)	%
Crude distillation, atmospheric	100	275	275	8
Crude distillation, vacuum	35	320	110	3
Catalytic cracking, fresh feed	28	1,400	400	11
Hydrocracking	4	2,000	80	2
Coking	6	1,200	75	2
Thermal cracking	3	700	20	1
Catalytic reforming	21	1,100	230	7
Alkylation, product basis	5	2,000	100	3
Hydrotreating	46	400	190	5
Others and offsites	100	2,000	2,000	57
Total refinery	100	11,395	3,480	100

aBasis: Total United States refining capacity, first of 1987. Cost: 1987 basis.

bSee the Petroleum Processes, Cost Indexes article to update these costs.

Costs are harder to nail down. Some reasonable estimates are given in Table 11. The relative capacity for each type of unit was fixed to match the relative capacity in existence in the United States at the first of 1987. The costs are also on a 1987 basis, although inflation has been changing these values rapidly.

An important item to notice is that more than half of the cost of a refinery is for materials and equipment other than those directly associated with specific petroleum processing. Some of these other items include storage, utilities, and environmental control systems. Land costs are excluded.

It should not be inferred that future construction will have the same cost distribution as shown in Table 11. The cost distribution in Table 11 is based on existing unit capacity. Future product demands will likely slant future construction in favor of one or another process with different relative unit costs based on future technology.

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Polymerization

Lyle F. Albright

Introduction

Polymerization conditions and processes often differ greatly for the production of different high polymers or even in some cases the same polymers. Careful control of the operating conditions is needed in all cases to obtain high-quality products in an economical manner. The high polymers considered here are those that have high molecular weights and that find uses as plastics, elastomers (or synthetic rubbers), synthetic fibers, adhesives, and surface coatings, such as paints or varnishes.

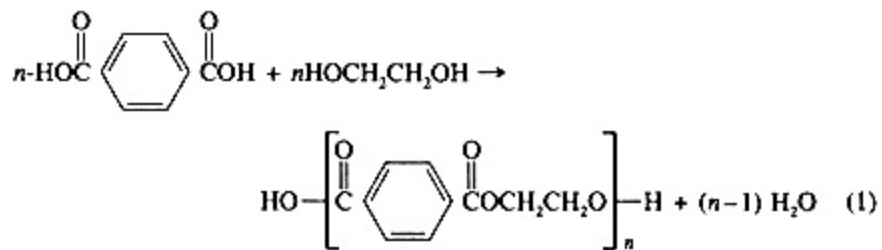
The operating conditions for the production of a polymer affect the rates of polymerization and also at least some of the following structural features of the polymer molecules: molecular weight, cross-linking, linearity of the molecule, branching, and stereospecificity. These features have a major effect on the morphology or packing abilities of the molecules and hence on the physical properties of the polymers. The relationship between structural features of the molecules and physical properties is considered in more detail later.

Chemistry of Polymerization

Based on the reactants used to produce the polymers, polymerizations are divided into two broad categories: polycondensations and addition polymerizations.

Polycondensation

Polyesters, polyamides (or nylons), polyurethanes, phenolics, urea resins, and epoxies are important examples of polycondensations. Often but not always, two or more reactants are employed, and the average functionality of the reactants must be at least two. A functionality of one is defined as the ability of a molecule to form a single chemical bond with another molecule. With a functionality of two, chemical bonds can be obtained with two other molecules. In the latter case, polymerization can occur and the polymer chain can increase in length (and molecular weight), forming so-called linear molecules. In theory at least, the molecular weight could increase to extremely high values if sufficient time is allowed for polymerization and if the ratio of reactive groups is correctly balanced. In the example shown next, terephthalic acid and ethylene glycol are reacted to produce poly(ethylene terephthalate) which is commonly referred to as PET. It is a polyester of considerable importance and finds uses as a textile fiber, film, and plastic (such as for soft drink bottles).



Both reactants have a functionality of two; the terephthalic acid has two $\begin{array}{c} \text{O} \\ \parallel \\ \text{COOH} \end{array}$ (COOH or acid groups) and ethylene glycol has two -OH (hydroxyl groups). The resulting polymer also has two functional groups; one is on each end of the linear molecule that can continue with time to react. The moles of terephthalic acid and of ethylene glycol must be identical or almost so to permit formation of a high polymer. A slight imbalance of the two reactants is sometimes deliberately employed to control the average molecular weight of the polymer. If a reactant with three or more functional groups is added, cross-linking between the polymer molecules occurs, resulting in gels with extremely high molecular weights. Cross-links increase the softening (and melting) points so that the polymers generally decompose upon heating before they soften sufficiently to be extruded or molded.

The rate (or kinetics) of polyesterification reactions can be correlated by mathematical expressions [1] similar to those of simple esterification reactions, which are reversible.

$$\frac{d(\text{ester group formation})}{dt} = k[\text{C}_{\text{COOH}}][\text{C}_{\text{OH}}] \quad (2)$$

where:

$[\text{C}_{\text{COOH}}]$ = concentration of acid groups (-COOH)

$[\text{C}_{\text{OH}}]$ = concentration of hydroxyl groups (-OH)

$k = (k')$ (catalyst concentration)

k' = kinetic rate constant, a function of both the type of catalyst and temperature

t = time

No term is included in this equation for the reverse reactions because the water is usually removed relatively rapidly from the reaction mixture by the use of a vacuum. Since $-d[\text{COOH}]$ equals $d(\text{ester group formation})$ and since $[\text{COOH}]$ essentially equals $[\text{OH}]$, the following simplification is possible when $[\text{C}]$ is substituted for $[\text{COOH}]$:

$$-\frac{d[\text{C}]}{dt} = k[\text{C}]^2 \quad (3)$$

This equation can be rearranged and integrated between the limits of $[C_0]$ (concentration at $t = 0$) and $[C]$ (concentration at time = t) to produce

$$\frac{1}{[C]} - \frac{1}{[C_0]} = k't \quad (4)$$

Similar kinetic expressions can often be developed for other polycondensations. Faster polycondensations occur as a rule with higher temperatures, higher concentrations of reactants, increased amounts of catalyst, and a more effective catalyst. Higher molecular weight polymers are obtained when these operating changes are made for polymerizations of the same length of time. If too high a temperature is used, however, undesired side reactions occur with loss of polymer quality [2, 3].

Addition Polymerizations

Polymers produced by addition polymerizations include polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(tetrafluoroethylene), often referred to as Teflon, poly(methyl methacrylate), whose tradenames include Plexiglas and Lucite, and several synthetic elastomers. To produce these polymers, select olefins or conjugated diolefins (or dienes, such as butadiene or isoprene) are polymerized. Simple olefins have functionalities of two (and produce chemical bonds with two other olefin molecules to form so-called linear polymers). Dienes potentially have functionalities of four, but the equivalent of only one double bond reacts as a rule so their functionalities are generally only two; hence they too generally form linear polymers.

Olefins and dienes polymerize by chemical steps very different from those of polycondensations. Intermediates formed during polymerization include free radicals, cations, anions, or catalytic complexes. The first three involve chain mechanisms in which the olefins (or dienes) add rapidly to a growing polymer chain. All the polymers mentioned earlier are produced commercially, entirely or in part, by free-radical polymerizations, except polypropylene and certain synthetic elastomers. Isobutylene is polymerized by a cationic mechanism at very low temperatures (often about -80°C) to produce butyl rubbers. Some speciality polymers are produced by the anionic route. Since the mid-1950s, coordinate catalysts, which are usually solids, have been employed to produce polymers of ethylene, propylene, butadiene, butadiene-styrene mixtures, and isoprene.

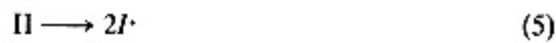
Free-Radical Polymerizations

Correlations have been developed using a mechanistic approach for free-radical polymerizations (Ref. 4 and Ch. 1 in Ref. 5). Since initiators are the most common method of producing free radicals, polymerizations using these compounds are discussed here in some detail. These initiators are often erroneously referred to as "catalysts", but they are not true catalysts

since they are not regenerated upon completion of the polymerization. Initiator fragments become part of the polymer molecule, but since they are present in minute quantities they have little effect on the physical properties of the polymer. Free-radical polymerizations of olefins or dienes are complicated by several intermediate reaction steps, as discussed next.

Initiation

Free radicals are produced in the initiation step. An initiator (Π) homolytically decomposes to form two free radicals (I^\cdot); these radicals are sometimes but not always identical. A resulting free radical reacts with a monomer molecule as follows:



where:

I^\cdot = free radical produced when the initiator fragments

M = monomer (olefin or diene)

IM^\cdot = free radical that starts the polymeric chain

The rate equation is as follows [1]:

$$\frac{d[I^\cdot]}{dt} = 2k_i[\Pi] \quad (7)$$

where:

k_i = kinetic rate constant

$[\Pi]$ = concentration of initiator

$[I^\cdot]$ = concentration of initiator fragments of free radicals

The rate at which polymeric chains (or IM^\cdot) are generated by the initiator is shown next:

$$-\left[\frac{d[M]}{dt}\right]_{\text{initiation}} = 2fk_i[\Pi] \quad (8)$$

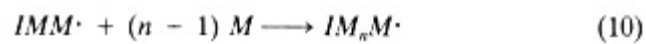
where:

f = fraction of initiator fragments that start a polymer chain

$[M]$ = concentration of monomer molecules

Propagation

Monomer molecules react rapidly by a chain mechanism to produce high-molecular-weight radicals as follows:



As each monomer adds one at a time to the chain, a higher weight radical is formed. Values of n increase as propagation continues, often reaching several thousand to at least a hundred thousand.

The rate equation for propagation assumes that k_p , the kinetic rate constant, is a function only of temperature and is independent of the viscosity of the reaction mixture. Even though the viscosity of a polymeric mixture is often very high and hence diffusion of reactants in the mixture is slow, this assumption is generally good, especially if the temperature is above the first-order transition temperature or the glass-point temperature.

$$-\left[\frac{d[M]}{dt}\right]_{\text{propagation}} = k_p [M][M^\bullet] \quad (11)$$

where $[M^\bullet]$ is the concentration of free radicals that results in polymer growth.

Since $-(d[M]/dt)_{\text{propagation}}$ is much greater than $-(d[M]/dt)_{\text{initiation}}$,

$$-\left[\frac{d[M]}{dt}\right]_{\text{total}} \simeq -\left[\frac{d[M]}{dt}\right]_{\text{propagation}} = k_p [M][M^\bullet] \quad (12)$$

Termination (Destruction of Free Radicals)

Coupling is a reaction between two free radicals (located on the end of polymer chains) to form a single polymer molecule (and hence a covalent bond is formed with the simultaneous destruction of two radicals). The rate expression is

$$-\left[\frac{d[M^\bullet]}{dt}\right]_{\text{coupling}} = 2k_{t,c} [M^\bullet]^2 \quad (13)$$

where $k_{t,c}$ = kinetic rate constant for coupling.

Disproportionation is also a reaction between two long-chain free radicals, but in this case an atom, often hydrogen, is transferred from one polymeric radical to the other. As a result, the two radicals are simultaneously destroyed, producing a double bond on the end of one polymer molecule and a saturated group on the end of the other. The rate equation

for disproportionation is

$$\left[\frac{d[M^\cdot]}{dt} \right]_{\text{disproportionation}} = 2k_{t,d} [M^\cdot]^2 \quad (14)$$

where $k_{t,d}$ = kinetic rate constant for disproportionation.

Combining equations for coupling and disproportionation [1]

$$-\frac{d[M^\cdot]}{dt} = 2[k_{t,c} + k_{t,d}][M^\cdot]^2 \quad (15)$$

Correlation for Rates of Polymerization

The concentration of M^\cdot in the mixture is estimated by the steady-state approximation in which the true rate of production of free radicals that cause polymerization equals their rate of destruction,

$$2fk_i [\Pi] = 2[k_{t,c} + k_{t,d}][M^\cdot]^2 \quad (16)$$

Rearranging:

$$[M^\cdot] = \sqrt{\frac{fk_i}{k_{t,c} + k_{t,d}}} \sqrt{[\Pi]} \quad (17)$$

The final rate expression can be developed as substitution:

$$-\frac{d[M]}{dt} = k_p [M][M^\cdot] = \frac{k_p \sqrt{fk_i}}{\sqrt{k_{t,c} + k_{t,d}}} [M] \sqrt{[\Pi]} \quad (18)$$

This equation correlates in most cases the rate of monomer disappearance and hence the rate of polymer formation. Faster rates of polymerization occur as the following occur:

1. Initiator concentration increases.
2. Monomer concentration increases.
3. Temperature increases; k_i increases significantly with temperature, whereas k_p , $k_{t,c}$, and $k_{t,d}$, which are for free-radical reactions, increase to a much lesser degree with temperature. Generally f changes little with temperature.

Factors Affecting the Molecular Weight of Polymer Molecules

The free radical in the growing polymer chain is sometimes transferred to the monomer (M), solvent (S), or initiator (Π). Growth in the polymer

chain is terminated, and a new polymer molecule is started. These chain transfer steps have rate constants designated $k_{tr,M}$, $k_{tr,S}$ and $k_{tr,I}$, respectively. Although these transfer steps do not affect the overall rates of polymerization, they result in shorter polymer chains, that is, lower molecular weight polymers. The following equation derived on mechanistic considerations is designated the kinetic chain length equation; the kinetic chain length γ is proportional to the average degree of polymerization (DP) or the molecular weight on a number or mole basis:

$$\frac{1}{\gamma} = \frac{k_{tr,M}}{k_p} + \frac{k_{tr,S}}{k_p} \frac{[S]}{[M]} + \frac{k_{tr,I}}{k_p} \frac{[I]}{[M]} + \frac{2\sqrt{(k_{t,c} + k_{t,d})fk_i}}{k_p} \frac{\sqrt{[I]}}{[M]} \quad (19)$$

This equation predicts how changes in the operating conditions affect the average molecular weight of linear polymer molecules produced by free-radical polymerizations. Lower molecular weights result when any of the following occur:

1. The concentration of the solvent increases, or a solvent is used that permits more rapid chain transfer.
2. The concentration of the initiator is increased, or a more active initiator is employed.
3. The temperature of polymerization is increased. As already mentioned, k_i increases rapidly with higher temperatures, whereas other rate constants increase less rapidly. At higher temperatures, more free radicals and more growing chains occur.

Branching

Branches on a linear polymer molecule have a major effect on the physical and sometimes the chemical properties of the polymer. Such branches are especially important with polyethylenes. More branching lowers the density of polyethylenes significantly since it results in poor packing of the molecules; it decreases the crystallinity and results in greatly reduced tensile strength.

Both short and long branches occur during free-radical polymerization of ethylene and to a lesser degree other olefins. Poly(vinyl chloride) (PVC), has some short branches [6]. To produce short branches, the free radical on the end of the polymer chain is transferred by an intramolecular mechanism [1], referred to as "backbiting." An atom, generally a hydrogen atom, transfers from the fifth carbon from the end of the chain, resulting in the free radical being positioned on the fifth carbon atom. Subsequent addition of olefin monomers to the free radical leads to n-butyl branches. Ethyl branches also form on the polyethylene molecule by a modified backbiting mechanism.

When intermolecular chain transfer occurs with a polymer molecule, the free radical is transferred to what had been an inactive polymer molecule. Propagation is then reinstigated on that molecule and a long branch results. Such chain transfer is most common when the concentration of polymer

molecules in the polymerization unit is high. For continuous-flow polymerization, chain transfer with the polymer is more important in a stirred autoclave or continuous stirred-tank reactor (CSTR) compared to polymerization in a long tubular reactor having essentially plug flow; there is on the average a lower concentration of polymer in the latter reactor.

Mathematical Modeling of Free Radical Polymerizations

Models have been developed with terms for initiation, propagation, termination, chain transfer, and backbiting for free-radical polymerization of olefins. They predict the rates of polymerization, degrees of polymerization, and branching of the resulting polymers; the physical properties of the polymers can then be predicted. Such models are often used for obtaining improved operating conditions and for developing polymers with improved properties (Ref. 4 and Ch. 1 of Ref. 5).

Cationic and Anionic Polymerizations

Rate and kinetic chain length equations similar to those just discussed can be developed based on mechanistic considerations for both cationic and anionic polymerization of olefins.

Polymerization of Olefins and Dienes Using Coordination Catalysts

In the 1950s, catalysts and processes were developed to produce several high polymers

1. High-density polyethylenes (HDPEs) have higher tensile strengths and higher densities compared to the polyethylenes that were produced previously [7]. In these processes, polymerization pressures are much lower; about 20 years later, processes were also developed to produce linear low-density polyethylenes (LLDPEs).
2. Polypropylene (PP) is extremely useful as a plastic since the repeating units are joined with an isotactic configuration [1].
3. Polymers of isoprene and butadiene are important synthetic rubbers. *cis*-Polyisoprene has properties similar to those of Hevea natural rubber. Both polymers are incorporated in premium-quality tires.
4. Random copolymers of ethylene and propylene are excellent oxygen-resistant rubbers.
5. Styrene-butadiene elastomers with improved properties.

Much improved catalysts have been developed in the last 510 years, and considerable effort is currently being made to finding even better ones [810]. Details of these catalysts are often closely guarded secrets since small

differences in catalyst preparation and properties lead to important changes in polymerization costs and/or polymer properties. Much more active catalysts containing titanium or chromium are now available, and some catalysts produce 50,000-100,000 weights of polymer per weight of "active catalyst." The important Ziegler or Ziegler-Natta catalysts are prepared by combining a titanium chloride with aluminum alkyl compounds. The active catalyst site is a Ti-C bond (an alkyl group is bonded to the titanium). Polymerization occurs when an olefin complexes with the Ti-C bond; this complex decomposes and the olefin is inserted in the chain, re-forming another Ti-C bond. This mechanism is often referred to as the "growing hair" mechanism because numerous olefins become incorporated one at a time into the growing chain.

Chromic oxide [11] or other chromium-containing compounds [12] are also effective catalysts. The support materials on which the active catalysts are deposited often activate the catalyst and affect the structure and molecular weight of the resulting polymers. McDaniel [13] has reported how modifications of a chromium catalyst have affected the molecular features of polyethylene products. During the polymerization of propylene, both the support and dispersion of catalyst on the support affect the stereospecificity (and specifically the isotacticity) of the resulting polypropylene.

During polymerizations on solid catalysts, the catalyst particles fragment and the active catalyst becomes finely dispersed throughout the polymer. With a highly active catalyst, so little catalyst is needed that there is no need to remove its residue from the polymer. Liquid catalysts can also be prepared, for example by using various vanadium salts; these catalysts can be used for polymerizations of ethylene or propylene. Such catalysts affect the stereospecificity of polypropylene, generally resulting in atactic varieties.

Solvents are commonly added to the polymerization vessel when coordinate catalysts are used to dissolve the monomer. In some cases, the polymer also dissolves in the solvent. The rates of polymerization increase in general with higher temperature, higher concentrations of dissolved monomer, and a more active catalyst. The molecular weight (or degree of polymerization) of the resulting polymer is controlled in several ways, including the choice of catalyst. Decreased molecular weights result at higher temperatures or when hydrogen is added to the reactor. Hydrogen is especially effective with Ziegler catalysts.

Relationship between Molecular Structure and Properties

The structures of the high polymer molecules have a significant effect on the physical properties and sometimes on the chemical properties of the polymer when used as a plastic, elastomer, or synthetic fiber, for example [5]. The molecular structure is controlled to a major degree by the operating conditions employed during polymerization, and hence these conditions

must be controlled correctly. Important features of the molecular structure that can be controlled are as follows:

Molecular weight: For linear-type molecules, increased molecular weights generally result in the following changes in physical properties: increased tensile strength, increased toughness or wearability, higher melt viscosities that result in slower rates of extrusion or molding, higher softening points, and lower solubilities in solvents.

Cross-linking: Cross-links or chemical bonds between polymer molecules occur when some reactants have functionalities greater than two. More cross-linking results in higher softening points, lower solubility in solvents, higher tensile strengths, and more brittleness. Cross-linking or vulcanization of rubber is an interesting example. A small amount of vulcanization is needed for the elastomers used in tires and overshoes, for example. With continued vulcanization, the rubber is converted to a plastic that has a high tensile strength but is brittle. Highly cross-linked polymers degrade or decompose at higher temperatures but do not soften sufficiently to be extrudable or moldable. During polymerization, care must be taken to prevent cross-linking in the polymerization reactor. If it were to occur, the polymer could not be easily removed from the reactor. The final and desired level of cross-linking generally occurs when the polymeric material is fabricated to produce the desired product.

Branching occurs during numerous polymerizations of olefins. For polyethylene, variations in the amount and type of branching have large effects on the physical properties. Polyethylenes with considerable branching have densities as low as about 0.91 g/ml, have much lower tensile strengths, are much more flexible, soften at lower temperatures, and are more permeable to gases than polyethylenes with densities in the 0.960-0.97 g/ml range [7]. The latter polyethylenes are at most only slightly branched. Branching results in poorer packing of the polymer molecules and decreases the crystallinity. For commercial polyethylenes, crystallinities vary from about 50 to 90% as indicated by either x-ray diffraction or infrared measurements. For polyethylenes, both short- and long-chain branching can be controlled by the method of polymerization and by the operating conditions used.

Stereospecificity features: Asymmetric carbon atoms are present in the polymer chain when certain olefins polymerize [1]. Such olefins include propylene, vinyl chloride, styrene, and methyl methacrylate. The resulting polymers can be isotactic, syndiotactic, or atactic. Isotactic and to a lesser extent syndiotactic configurations result in molecules that pack better and hence have higher densities; because of the improved packing, the tensile strengths are sometimes substantially higher such as is true particularly for polypropylene. Isotactic polypropylene is of great industrial importance, whereas the demand for atactic polypropylene is much more limited. For polystyrenes, however, the properties of the atactic and isotactic types differ only slightly. Atactic polystyrene is the only type of commercial importance. Polymerizations of butadiene or isoprene

result in polymers with double bonds in the chain in either the cis or trans configuration. Cis-polyisoprenes are highly suitable for tires. With trans configurations, however, the polymers are not suitable for tires but are for golf balls. Variations in polymerization methods often permit large changes in the stereospecificity of the polymer molecules.

Polymerization Procedures

Polymerization procedures have been characterized for many years as bulk (or mass), solution, emulsion, or suspension polymerizations. The distinction between these four categories is sometimes blurred, and some polymerization processes do not really fall into any of the four categories. Process equipment and conditions often differ significantly for various polymerizations.

Bulk Polymerizations

Bulk polymerizations are those in which only the monomer (or reactants) plus possibly an initiator or a catalyst are added to reactor vessel. In other types of polymerizations, a solvent or water is also added. Bulk polymerizations often produce higher purity polymers and in general require simpler separation procedures. Such small amounts of initiator or catalyst are generally employed that separation of initiator or catalyst residue is unnecessary. Temperature control is sometimes a special concern in bulk processes, especially when the resulting mixtures of polymer and monomer have very high viscosities and the exothermic heat of polymerization is hard to remove.

Bulk processes are divided into the following types: the polymer and monomer are completely soluble in each other; the polymer and monomers are essentially immiscible, as follows:

1. Solid polymer-liquid monomer slurries
2. Solid polymer-gaseous monomer mixtures

Important industrial examples of these types are described next.

Bulk Polymerization of Styrene [14, 15]

Styrene and polystyrene are completely miscible in each other, and the viscosity of the reaction mixture increases as the concentration of dissolved polystyrene increases. At low styrene conversions, the viscosity is low, similar to that of gasoline. When polymerization is almost complete, the viscosity of the reaction mixture may be as high as 1.0 million cP (depending on the temperature and the molecular weight of the polystyrene).

Batch reactors were used in the 1930s and 1940s for the bulk polymer-

ization of styrene. Agitation was sometimes provided. Temperature control was always a key factor since heat transfer in the viscous mixtures is poor. Large temperature variations sometimes occurred in the batch reactors because of the high exothermicities of polymerization, and hence polystyrenes with a wide range of molecular weights generally resulted.

Most current industrial reactors for production of polystyrene are operated in a continuous-flow mode. Long cylindrical reactors with the agitator shaft located at the axis are frequently employed; several agitator blades are positioned on the shaft. Heat transfer surfaces are provided on the walls and sometimes in internal portions of the reactors. Little backmixing of reactants occurs in these reactors; some are positioned vertically, but others are horizontal. A reactor is generally operated so that the temperature of the reaction mixture increases as it passes through it. Near the inlet, temperatures are often about 100–110°C, but at the outlet they are sometimes 200°C or higher. Three reactors are frequently connected in series. The first reactor is designed for the relatively low viscosity mixtures, and temperature control is relatively easy to maintain. In the second reactor, temperature control is often most critical since viscosities are considerably higher and heat transfer resistances are greater. Sufficient styrene is still present to permit rapid rates of polymerization, however, especially if the temperature becomes slightly higher than design values. Runaway reactions and explosions have been experienced in the past in this reactor. In the third reactor, the viscosities are extremely high but little styrene is available for further polymerization; temperature control is easier to maintain.

The mixture from the last reactor contains a small amount of styrene plus usually some ethylbenzene (or other solvent). Ethylbenzene is often added with the styrene feed since it reduces the viscosity of mixtures in the reactor and hence reduces the resistance to heat transfer. Concentrations of ethylbenzene are usually low so that this polymerization is generally still referred to as bulk polymerization, not as solution polymerization (which uses appreciable amounts of solvent, as discussed later). The unreacted styrene and ethylbenzene (if used) are next separated from the molten and highly viscous polystyrene. To do this, the molten mixture is formed into numerous filaments or thin films to obtain a large liquid/gas interfacial surface area. The filaments or film is subjected to low pressures (or vacuum), causing the styrene and solvent to vaporize. The resulting polystyrene is molten (with a high viscosity) and is often pelletized to provide particles suitable for extrusion or molding operations.

Polystyrene can also be formed by casting. Liquid styrene is added to a mold. Styrene is sufficiently reactive even with no initiators present so that it polymerizes within days or weeks at essentially ambient temperature. If the temperature is increased, polymerization is more rapid. Casting is also used to produce poly(methyl methacrylate).

High-Pressure Polymerization of Ethylene [15]

Ethylene is bulk polymerized within 1040 s at pressures of 1,2003,000 atm and at temperatures ranging from 150 to 340°C; mixtures are produced

containing 1540% low-density polyethylenes (LDPEs) and the remainder ethylene. Figure 1 is a simplified flowsheet for the production of LDPEs using a tubular reactor. The densities of these extremely important polymers can be varied from about 0.910.935 g/ml depending primarily on the pressure employed. At the conditions employed, the ethylene gas is compressed to densities of 0.450.6 g/ml, that is, densities approaching those of liquid hydrocarbons. At the higher reaction temperatures, the ethylene and polyethylene product are completely miscible; at lower temperatures, polyethylene-rich and ethylene-rich phases sometimes form. Two types of continuous-flow reactors are used.

Tubular reactors are generally 38 cm in inner diameter, are often several hundred meters in length, and have wall thicknesses of 25 cm. A reactor is constructed with several straight sections of tubing positioned in parallel and connected with U bends. The internal diameters of the tubes in a given reactor sometimes differ, with the larger diameters at and near the exit end [16]. The flow velocities of the reaction mixtures are relatively high so that residence times in the reactor are often about 3040 s. The tubes are jacketed, and the ethylene is first preheated to reaction temperature. The initiator, which is often oxygen (in air), is then introduced and polymerization results; the heat of polymerization is transferred to the jacket. Temperature variations at 2040°C often occur in the localized regions in which polymerization occurs. Additional ethylene and initiator are frequently added at one or more intermediate points along the flow path; in which case more than one polymerization zone occurs in the reactor.

Autoclave reactors are essentially CSTR reactors. Sometimes more than

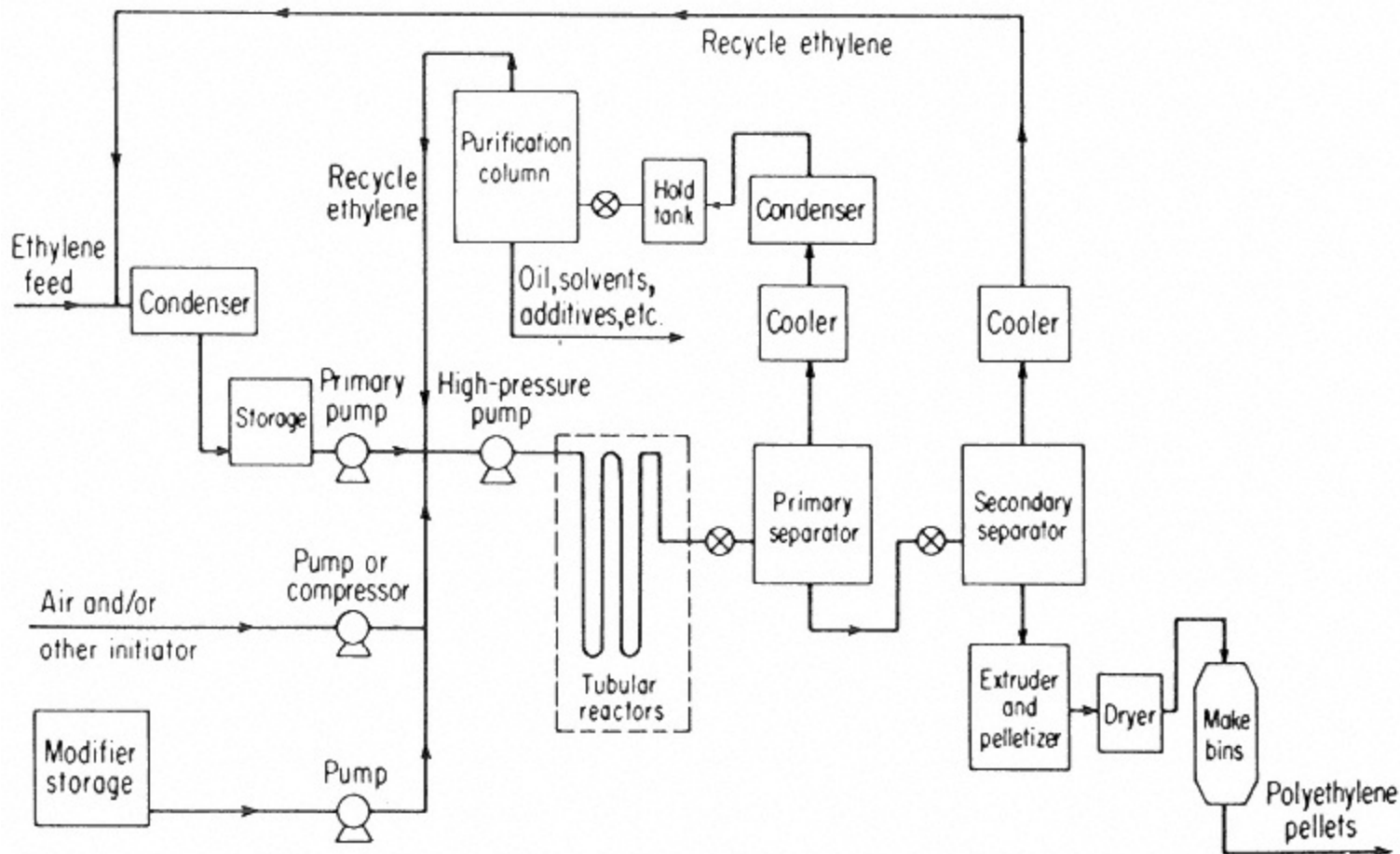


Fig. 1
High-pressure process for production of low-density polyethylene.
(From Ref. 15 with permission of Krieger Publishing Co.)

one autoclave reactor or reactor compartment is provided in series. The flowsheet of a process using an autoclave reactor is similar to that shown in Fig. 1. Because of the very thick walls required to withstand the high-pressures, little heat can be transferred from this type of a reactor and each is operated essentially adiabatically. Heat exchangers are sometimes provided between reactors when more than one is used in series. The molecular structure of the LDPE produced in autoclave reactors differs somewhat from that produced in tubular reactors.

Mixtures of ethylene and LDPE leave the polymerization reactors. Several years ago, the exit stream often contained 1520% LDPE; 1520% of the ethylene was polymerized per pass through the reactor. Newer units often produce mixtures containing 3040% LDPE [16]. Increased conversions of ethylene per pass result in lower operating costs per unit weight of LDPE because the production capacity of a reactor is drastically increased and, the amount of unreacted ethylene is greatly reduced and hence the costs of recovering, recompressing, and recycling it are reduced.

To separate the unreacted ethylene from LDPE, the pressure is reduced first in the primary separator and then further reduced in the secondary separator to about 150 atm (see Fig. 1). The resulting LDPE has a high viscosity. The desorbed ethylene is then cooled, sometimes condensed, purified if needed, and finally recompressed to reaction pressures and recycled to the reactor. Compressors for LDPE plants are large and expensive to operate. Energy requirements for these compressors are often 6,00010,000 hp per 100 million lb LDPE per year. This polyethylene product is generally extruded, pelletized, and dried before storage and sale.

Gas-Phase Polymerization of Ethylene and Propylene [15]

The Unipol process, which operates in the continuous-flow mode, was commercialized by Union Carbide Corp. for the production of high-density polyethylene (HDPE) in about 1970, linear low-density polyethylene in the late 1970s, and polypropylene in the early 1980s. Figure 2 is a simplified flowsheet for HDPE production. This gas-phase process is a bulk polymerization process in which the solid polymer particles are in contact with gaseous monomer [17]. Temperatures in the reactors are usually in the range of about 80100°C. At such temperatures, the polymer particles, which are quite crystalline, have little or no tendency to agglomerate or stick together. These temperatures are well below the first-order transition temperatures (or melting points of the crystalline polymers) at which agglomeration is a problem. Pressures in the reactor are often in the 1821 atm range. The distributor plate on the bottom of the polymer bed must provide uniform flow of the upflowing monomer stream.

Since highly active catalysts are employed, only small amounts of catalyst are needed. The catalyst is often present in the final polymer in concentrations of 1020 ppm by weight. In the Unipol reactor, the upflowing monomer (ethylene and/or propylene) contacts and fluidizes the granular polymer particles. Polymerization occurs with a growth

in both the size and number of the polymer particles. In the reactors of other gas-phases processes, a

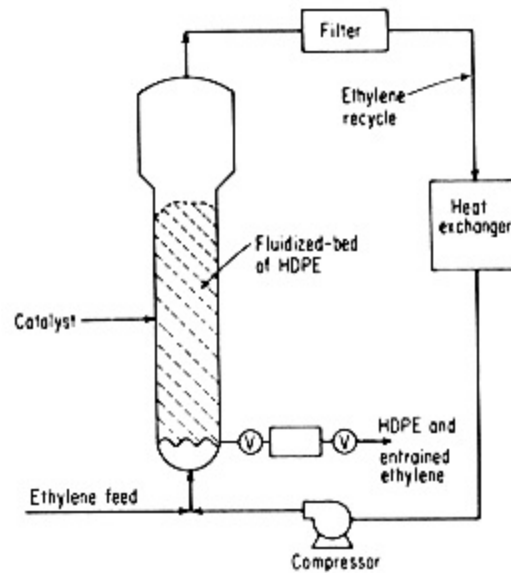


Fig. 2
Unipol process for production of HDPE.
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mechanical agitator or blender is sometimes used to provide contact between the solid particles and the monomer gas stream.

In the Unipol process, the fluidized bed is in a vertical cylindrical reactor. This bed is often about 1215 m high and in larger reactors has a diameter of about 4.55.0 m. Figure 3 is a photograph of two Unipol reactors. The top of the reactor has a larger diameter and is bulb shaped so that the gas velocity there is reduced, permitting the granular polymer to separate from the upflowing gases. The same reactor is suitable for production of HDPE, LLDPE, and PP. In producing LLDPE and sometimes HDPE, a comonomer is used in addition to ethylene. Comonomers include 1-butene, 1-hexene, and 1-octene that result in short branches on the copolymer chain. The densities and physical properties of the HDPE and LLDPE are controlled by the amount and type of comonomer used.

The unreacted gaseous monomer (plus comonomer when used) is cooled to remove the heat of polymerization, recompressed, and then recycled to the bottom of the reactor. Approximately 2% of the monomer reacts per pass, and hence the volumes of gas recycled are large; however, there is only a relatively small pressure drop as the gases transverse the bed. The compressor costs for the feed and recycle ethylene are moderate compared to those of the high-pressure processes used for the production of LDPE, as just described.

Larger polymer particles in a gas-phase process accumulate in the bottom of the bed, and some polymer particles plus small amounts of unreacted monomer are semicontinuously removed from the bottom of the reactor. Once outside the reactor, the monomer is easily separated by gravity from the solid polymer particles. Relatively little monomer adsorbs on or is re-

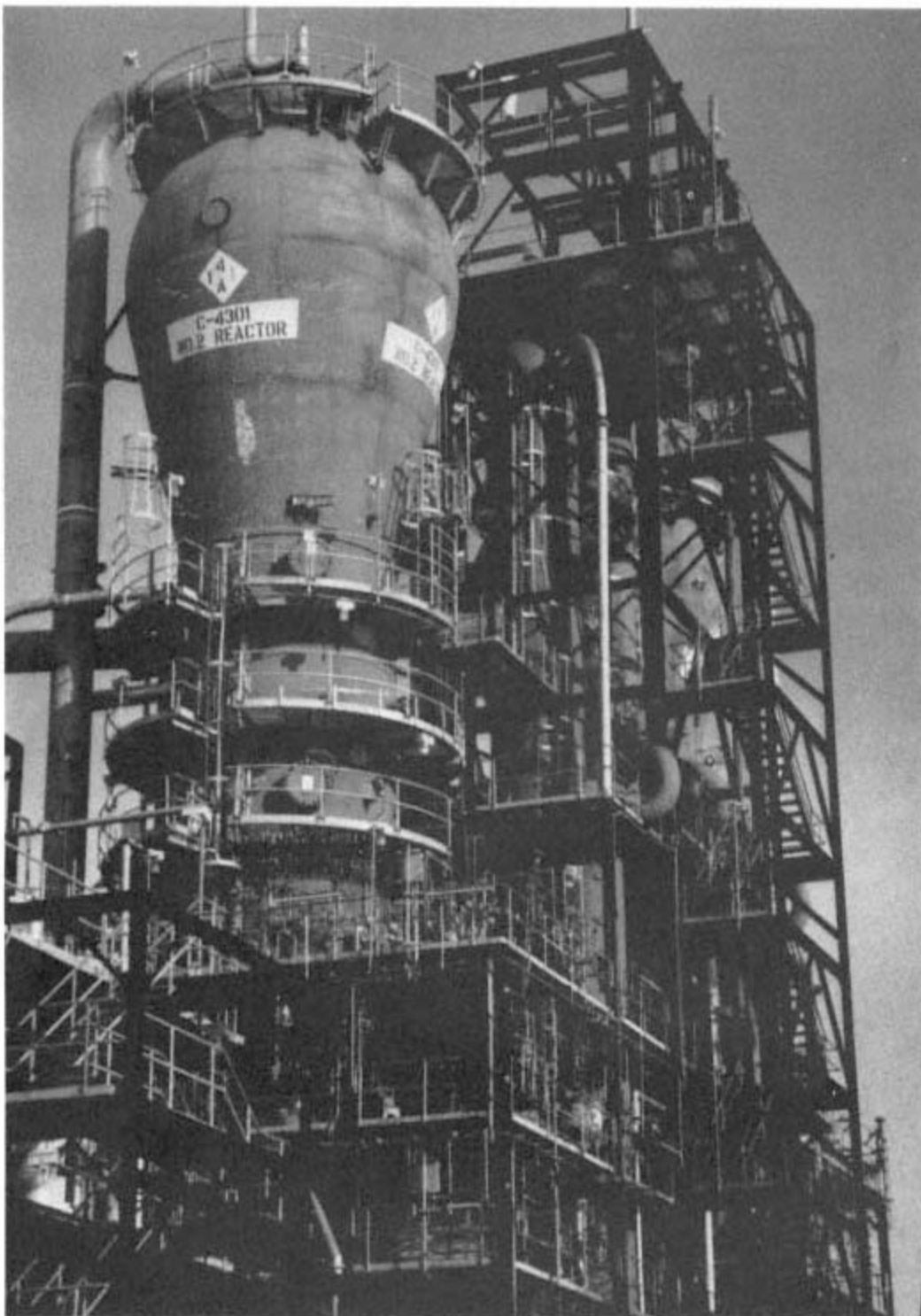


Fig. 3
Unipol reactors at Union Carbide plant.
(From Ref. 15 with permission of Krieger Publishing Co.)

tained in the porous polymer particles. The resulting polymer particles are often spherical (see Fig. 4) and frequently do not require pelletizing for subsequent fabrication processes. Such additives as antioxidants, dyes, or pigments are sometimes incorporated in the polymer particles following polymerization.

Economic benefit would result if significantly more than 2% of the feed olefins could be polymerized per pass. In such a case, the production capacity of the reactor would be increased and compression cost would be further reduced. Based on the flowsheet in Fig. 2, the heat of polymerization is essentially balanced by the sensible heat added to the feed gases as they are heated to the reaction temperature. The following modification is used in at least some commercial Unipol reactors to provide increased heat removal from the reactor and to permit higher conversions per pass. A fairly volatile liquid, such as relatively light paraffin or isoparaffin, is also added to the reactor. Part of the heat of polymerization then provides the latent heat of vaporization of this liquid. This additive is later condensed in the heat exchanger and then recycled. Other options that have been considered for improved heat removal from the reactor include jacketing the reactor and providing a heat exchanger for the feed stream to the reactor.

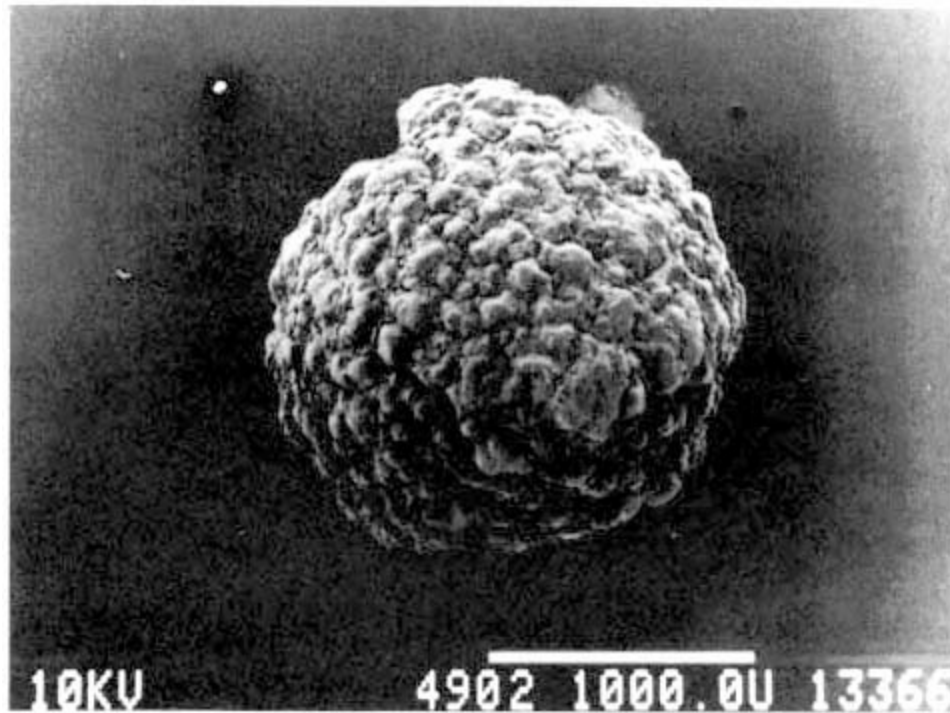


Fig. 4

Microphotograph of granular polyethylene particle produced in Unipol process.
(From. Ref. 15 with permission of Krieger Publishing Co.)

Bulk Polymerization of Vinyl Chloride [15, 18]

A bulk polymerization process is used in the United States to produce about 10% of the PVC. This batch process was initially called the Saint-Gobain, later the Pechiney-Saint Gobain, still later in the Rhone-Poulenc, and currently the Chloé Chemie process, as various industrial reorganizations occurred. PVC is only slightly soluble in liquid vinyl chloride, and a slurry of solid PVC particles and liquid vinyl chloride forms during the initial stages of polymerization in the first batch reactor (often called prepolymerizer). An active initiator is employed so that 710% conversions of vinyl chloride to PVC are realized within about 30 min when the temperature is controlled at 6275°C. A jacket is provided to remove the exothermic heat of polymerization. The PVC particles have large porosities so that considerable vinyl chloride is absorbed or retained in the particles. Agitation in the reactor and pumping of the slurries becomes difficult at conversions greater than 10%.

The slurries from the prepolymerizer are transferred to the second reactor (or autoclave), which is equipped with an incurvated agitator blade or ribbon blender. A horizontal vessel was used until the late 1970s, but a vertical vessel, as shown in Fig. 5, is now recommended. The temperature in the autoclave is controlled by heat transfer to the jacket, water cooled impeller, and external reflux condenser. The agitator blade turns slowly, but it provides good contact between the solid PVC particle, liquid vinyl chloride that wets the particles, and/or gaseous vinyl chloride. The reaction in the autoclave is usually completed within 34 h. Polymerization is stopped by releasing the pressure. The residual vinyl chloride is removed by vaporization and is eventually recycled to a reactor.

Some PVC sticks on the walls of the autoclave, and an autoclave is generally cleaned after most runs. Hydraulic high-pressure devices are installed for water washing.

The solid PVC particles from this mass polymerization unit are highly porous, and they effectively adsorb liquid plasticizers, which are frequently added to PVC. The size of the final polymer particle is controlled mainly by the level of agitation provided in the prepolymerizer. The bulk density or porosity of the final PVC particles is controlled by the temperatures in both reactors and by the final degree of conversion of the vinyl chloride in the second reactor.

Bulk Polymerization of Propylene [15]

Some polypropylene is produced using a bulk process in which solid granules of polypropylene are suspended in liquid propylene. The propylene acts in this process both as a reactant and as a liquid to obtain solid-liquid slurries. This process is very similar to slurry processes using solvents to be discussed later for the production of LLDPE, HDPE, and PP.

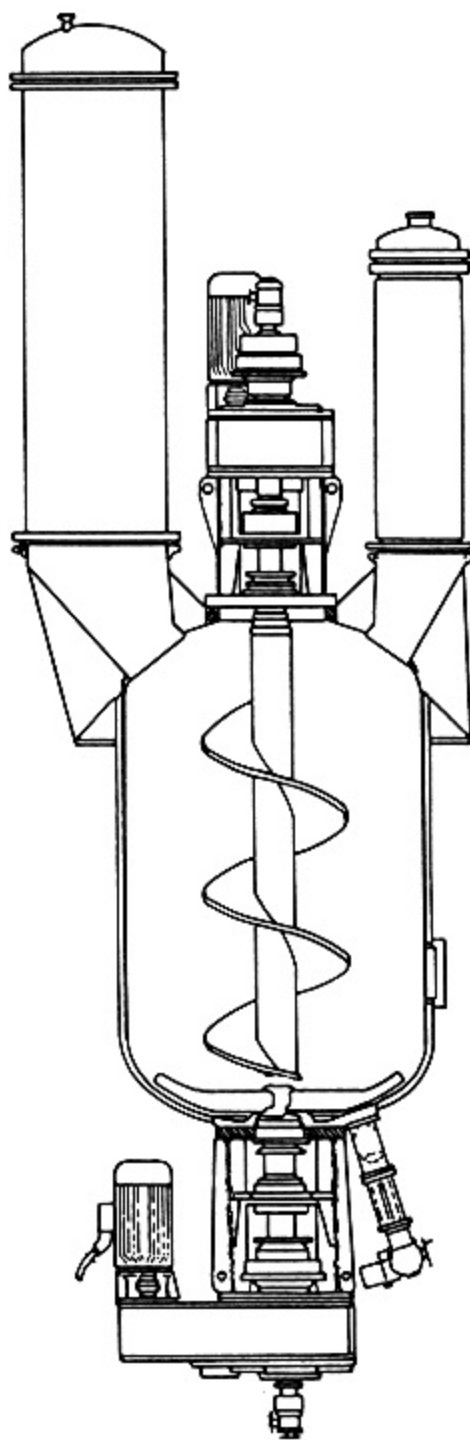


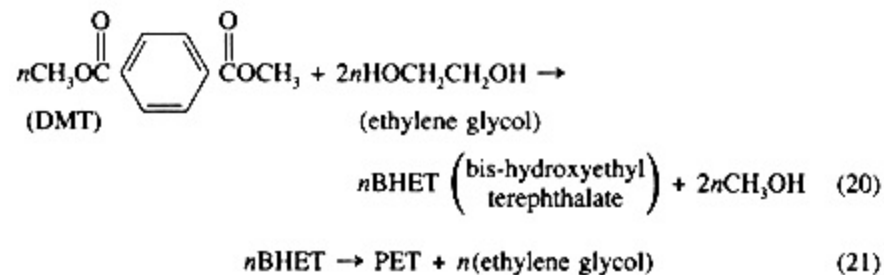
Fig. 5
Vertical autoclave used bulk polymerization
of vinyl chloride.
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Production of Poly(ethylene Terephthalate) and Nylons

These two condensation polymers, which are widely used as both synthetic fibers and plastics, were produced in the 1940s and 1950s in batch autoclaves [1]. More recently, continuous-flow systems have been developed and are often used. These bulk polymerizations differ in several respects from the polymerizations mentioned earlier.

The production of PET and nylons involve equilibrium reactions, but the equilibrium constants for nylons are much higher than those for PET. The production of the former is discussed here in most detail [3]. PET crystallizes sluggishly, and its uses as a plastic were limited until methods of promoting crystallization and simultaneously obtaining high molecular weights were developed. Nucleating agents that increase the rates of crystallization are often added in small quantities when plastic items are fabricated. Finely divided PET crystals or poly(methyl methacrylate) are two examples of effective nucleating agents. The desired amount, type, and orientation of the crystallites differ between plastic or fiber products for both PET and nylons.

PET is produced by reacting either terephthalic acid or dimethyl terephthalate (DMT) with ethylene glycol. DMT was used almost exclusively in the 1940s and 1950s since there were then problems in adequately purifying terephthalic acid. Purified terephthalic acid is now available, and it is being used to an increasing extent. The reactions with DMT can be divided into two steps as follows:



When a batch autoclave is employed, DMT is added as a melt along with liquid ethylene glycol. Terephthalic acid, however is added as a granular solid slurried with excess ethylene glycol. The temperature of the batch reactor is slowly raised as the run progresses, and the pressure is simultaneously lowered. Methanol and excess ethylene glycol are removed by vaporization for polymerizations using DMT, and water and excess ethylene glycol are removed in runs using terephthalic acid. Factors of importance during the production of PET are as follows:

1. Mass transfer steps for the removal of water or of ethylene glycol are generally rate controlling, especially in the final stage of polymerization.

An agitator in the autoclave promotes these transfer steps, but because of the high viscosities that occur, there is a rather slow turnover.

2. Pressures as low as 0.2 mm Hg (absolute) are often employed during the final stages of polymerization to remove the water or excess ethylene glycol as gases.

3. Undesired side reactions occur at especially higher temperatures, such as 280°C and higher [2, 3]. Yet temperatures in the 280-290°C range are often needed to obtain the desired degrees of polymerization. The residence times of reactants in batch reactors are generally controlled to less than 812 h.

4. Catalysts are used to increase the rates of polymerization and of transesterification. Antimony(III)oxide is a typical polymerization catalyst, and manganese acetate is a good catalyst for ester interchanges. Other catalysts have been reported in the patent literature.

Continuous-flow polymerization units for the production of PET generally consist of three to six vessels or reactors connected in series [19], and each is operated under somewhat different conditions. Figure 6 shows the four vessels used by E.I. duPont de Nemours and Co. when DMT is reacted with ethylene glycol. Most methanol (with DMT runs) and most water (with terephthalic runs) is removed in the initial vessels. Ethylene glycol is vaporized in significant amounts in the latter reactors, which are at higher temperatures and lower pressures. In a modern flow process, high-molecular-weight and high-quality PET can be produced with few side reactions.

Nylons 6,6, 6, 6,10, and 6,12 are the most important nylons produced commercially. For batch processes, stirred autoclaves are used. Flow pro-

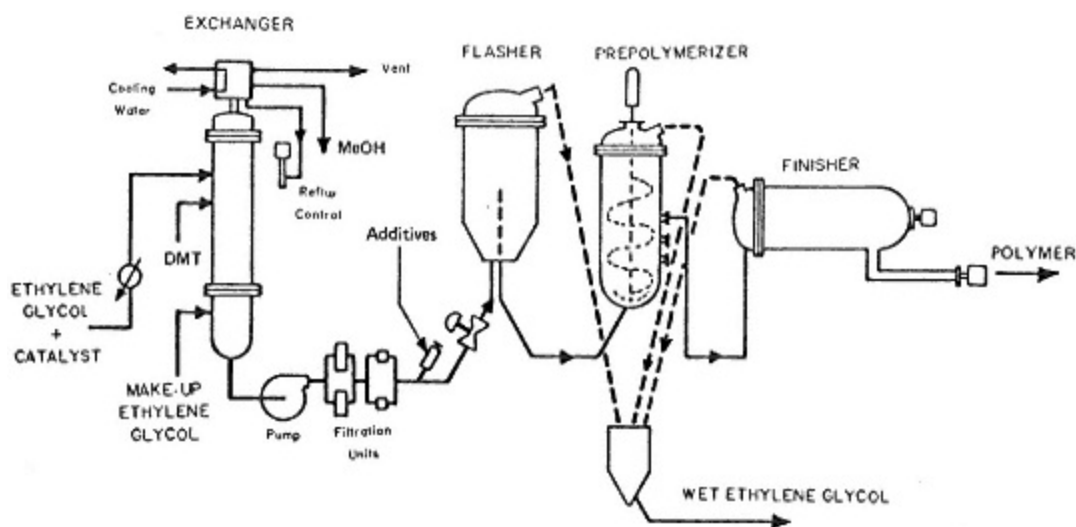


Fig. 6

Continuous-flow process for production of poly(ethylene terephthalate) using diethyl terephthalate.
(Courtesy of E. I. duPont de Nemours and Co., Inc.)

cesses employ several reactors in series. Steffan et al. [20] have reported on a flow thin film model for the polymerization of nylon 6,6. Rapid removal of the water (as steam) is of importance in the process.

Solution (or Solvent) Polymerizations [15]

A solvent is used in numerous polymerization processes to dissolve or dilute the monomer or reactants. Sometimes the resulting polymer is also dissolved, but not in other cases. Most processes employing coordination catalysts use a solvent, and some processes using initiators or other catalysts do, too.

Polymer Dissolves in Solvent

HDPE, LLDPE, PP, and several synthetic elastomers are produced in processes using both a solvent and a coordination catalyst. C₅C₇ paraffins are frequently used solvents for the polymer. Light aromatics are rarely used, however, because of toxicity considerations. In these processes, the monomer (or comonomers), solvent, and catalyst are added to the reactor. Comonomers used in the production of LLDPE include 1-butene, 1-hexene, and 1-octene. These comonomers may be used in small amounts for the production of HDPEs. Ethylene is sometimes used in relatively small amounts as a comonomer in PP production. The solution leaving the reactor frequently contains 10–15% dissolved polymer. One or more reactors are used in series when continuous-flow operations is employed.

HDPE, LLDPE, and PP are crystalline to an appreciable extent, and to dissolve them in the solvent, polymerizations are made at temperatures above the first-order transition temperature (the melting point of the crystalline polymer) using rather effective solvents. For polyethylene, polymerization temperatures are often controlled within the range of about 140–250°C. Polypropylene has a higher first-order transition temperature, and polymerization temperatures are often 160–250°C. Polymerization temperatures in these solution processes are considerably higher than those in the gas-phase processes (already discussed) and in the slurry process (discussed later). Because of the relatively high temperatures used, the average molecular weight of the polymers produced in the solution processes are often lower than those of polymers in lower temperature processes. The higher temperatures, however, result in high rates of polymerization, and relatively small reactors can be used for solution polymerizations. Synthetic elastomers are not crystalline, however, and they are soluble in solvents even at low temperatures. Relatively low temperatures are frequently used to obtain the high-molecular-weight elastomers that are generally preferred.

The solvent and unreacted monomers (or comonomers) are usually separated from the polymer (or copolymer) by a combination of flashing and stripping. Lowering the pressure permits most of the unreacted monomer and some of the solvent to flash off. A stripping column is often used to remove the remainder of the solvent. The solvent is recovered, purified if necessary, and then recycled to the reactor. Provisions are often included

to "deactivate" the catalyst entrapped in the polymer by contacting the polymeric product with an alcohol or steam. When less active catalysts are used, relatively large amounts of catalyst residues must be removed from the polymer. With the more active catalysts now available, the amount of residues are very small and separation is usually unnecessary.

Slurry Processes

Slurry processes are popular for the production of HDPE, LLDPE, and PP. In these processes, a slurry of the solid granular polymer particles and the solvent (plus dissolved monomer) forms. Polymerization occurs primarily on and in the particles, which grow in size. Slurry processes are operated at temperatures substantially less than the first-order transition temperatures of the crystalline polymers being produced. At low temperatures, only a small amount of polymer is dissolved in the solvent. The polymers that dissolve are those that are more easily dissolved, including the low-molecular-weight polymers (the waxes and greases), the more branched or lower density polymers (in the case of particularly polyethylene), or the atactic polymers (in the case of polypropylene). Relatively light paraffins or isoparaffins, such as isobutane, are often used as solvents since the polymers are less soluble in them than in the heavier paraffins. Slurry processes generally operate at lower pressures compared to the solution processes because of the lower temperatures employed. The slurry processes just described are very similar to the bulk process mentioned earlier for PP production; in that process, PP particles are suspended in liquid propylene.

Loop reactors are employed by several companies for the continuous-flow production of HDPE, LLDPE, and PP. These companies include Phillips Petroleum Co., Solvay et Cie, and Quantum. The reactor consists of a loop of tubing through which the reaction mixture (or slurry) is repeatedly recirculated at velocities of about 3.310 m/s. Loop reactors are constructed with relatively long straight sections of tubing connected by bends and short sections of tubing. Larger loop reactors have an internal diameter of about 5065 cm; the length of path around the loop is often 150165 m. Some loop reactors contain two loops joined in series and with the loops positioned vertically [11, 15, 21], as shown in Fig. 7. Other loop reactors contain only a single loop, which is positioned horizontally at essentially ground level. The heat of polymerization is transferred to a coolant in the jacket on the outer wall of the tubing. Care must be taken not to have too large a temperature difference across the wall since too low a skin temperature on the inner wall of the tubing promotes undesired sticking of the polymer particles.

Several companies use stirred autoclaves as polymerization reactors. These reactors are jacketed to provide adequate heat transfer. They are sometimes used for batch polymerizations but are more commonly used for continuous-flow polymerizations. In the latter case, two or more reactors are frequently joined in series. Flow processes usually result in lower operating costs.

Settling legs are generally provided at the bottom of the reactor (see

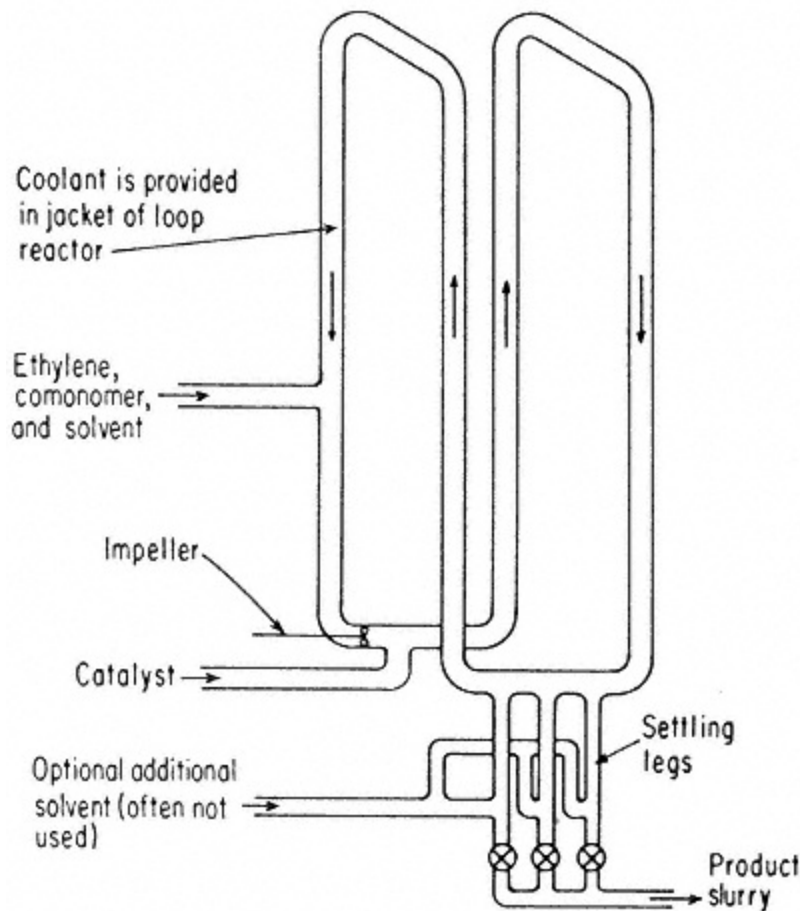


Fig. 7

Loop reactor used for production of HDPE.

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Fig. 7) to provide partial separation of the solvent and polymer particles [22]. Slurries containing as much as 50-70% solid polymer particles are obtained in these legs. The exit slurry from the settling leg is centrifuged to separate most of the solvent from the porous polymer granules. These granules are then washed with clean solvent. The solvent that remains attached to or that fills the pores of the granular particles is removed by evaporation. Less energy is needed for evaporation when light solvents, such as isobutane, are used. The solution separated from the polymer particles contains small amounts of dissolved polymers. It is either recycled to the polymerization reactor or is sent to a separation unit to recover the soluble polymer fractions. After such a separation, the recovered solvent is recycled to the reactor.

Slurry processes tend to have substantially lower operating costs compared to those processes in which the polymers dissolve in the solvents. Separation of the polymer and solvent is much simpler and cheaper in the slurry process. When certain catalysts, such as chromium oxides, are used in slurry processes, relatively low-molecular-weight (or high-melt-index) polyethylenes are difficult if not impossible to produce. With a solution process, however, no such problems occur because of the higher polymerization temperatures employed. The slurry process offers a convenient method of removing waxes and greases if they are formed in substantial amounts and if removal would improve the properties of the resulting polymer.

Suspension and Emulsion Polymerizations [15]

Numerous olefins and dienes are polymerized by free-radical polymerizations using suspension or emulsion polymerization process [1]. The reactors (or polymerization units) for both types of polymerization are often similar. Although continuous-flow processes have been proposed for suspension polymerizations, all known industrial suspension processes use batch reactors, such as that shown in Fig. 8. A mechanical agitator is provided in these reactors to disperse the liquid olefin (or diene) as droplets throughout the continuous water phase. Similar batch reactors are used for emulsion processes, but flow reactors are sometimes used. There appear to be at best only relatively small economic advantages to flow processes for either suspension or emulsion polymerizations. Most companies produce several types of a specific plastic, and each type can generally be obtained readily in batch processes. In a flow reactor, however, off-specification products are likely formed while a switch is made from one type to another.

Emulsion polymerizations (Refs. 1 and 23 and the first part of Ref. 24) generally produce polymers with very high molecular weights. As a consequence, emulsion processes are often used for the production of polymers requiring high molecular weights, such as styrene-butadiene elastomers (or SB elastomers) and poly(tetrafluoroethylene), which is often referred to as Teflon.

For both emulsion and suspension polymerizations [1], two liquid phases occur: a water phase, which is the continuous phase, and a dispersed organic-

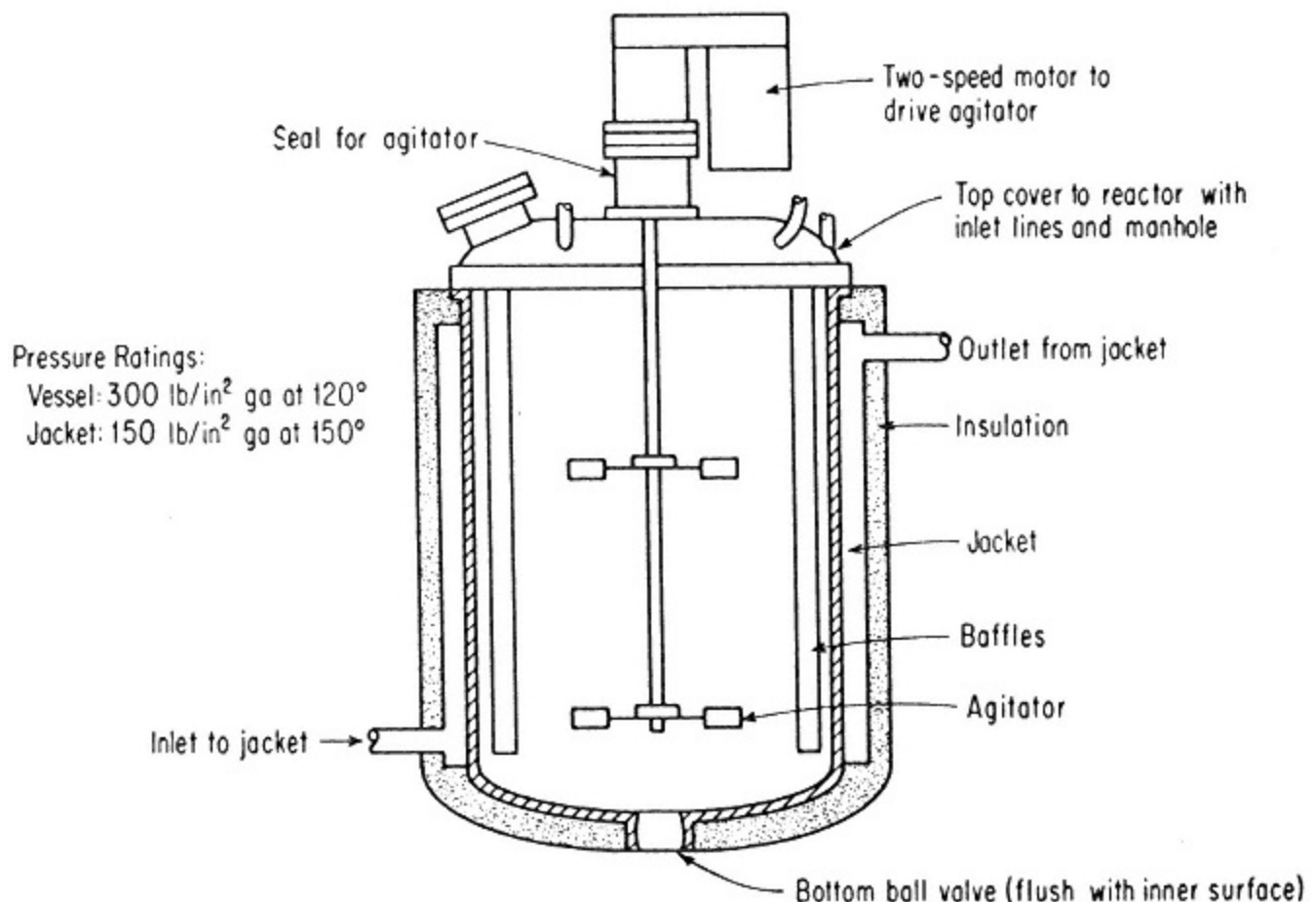


Fig. 8

Batch reactor used for suspension or emulsion polymerization.
(From Ref. 15 with permission of Krieger Publishing Co.)

rich phase, which is initially a mixture of monomer and initiator. The weight ratio of water to monomer frequently ranges between 1.2 and 1.75. A surfactant or dispersing agent is added in both types of polymerizations. For suspension polymerizations, the amount and type of surfactant affects both the size and number of dispersed droplets or polymer particles (when polymerization is completed). The surfactant regulates the agglomeration and dispersion of these droplets, especially during those phases of polymerization when they become sticky. In some cases, such as for the production of poly(vinyl chloride), the surfactant also affects the porosity of the solid polymer particles produced. About 0.51.0% by weight surfactant is often used, based on the monomer used.

For emulsion polymerizations, more surfactant is employed, often in amounts of 1.53% by weight. Part of the surfactant accumulates around the dispersed monomer droplets, and the remainder forms numerous micelles in the water phase. These micelles are clumps of surfactant molecules that capture some of the free radicals formed when the water-soluble initiators fragment. Propagation (or polymerization) reactions start in the micelles, and polymer particles are formed as more olefin (or diene) molecules react. Since the number of free radicals in a growing polymer particle is very small, termination steps by coupling or disproportionation are rare and the polymers produced have very large molecular weights.

For suspension polymerization, monomer-soluble initiators are used, and most polymerization steps occur in the dispersed (or organic-rich) phase. Unfortunately, a small amount of initiator is also soluble in the water phase; this portion of the initiator leads to the formation of some polymers that are not adequately protected by the surfactant or stabilizer. Unprotected polymer frequently collects on or fouls the inner walls of the reactor. When this occurs, the polymer quality tends to decrease and poorer heat transfer results in the reactor. This problem is minimized by selection of initiators that are less soluble in water.

Key features of the reactor design are as follows:

1. Heat transfer provisions. All or at least a significant fraction of the heat of polymerization and of the heat generated by agitation is transferred from the water phase in the autoclave, through the wall of the reactor, to the coolant (usually water) in the jacket. Water-cooled baffles and an external reflux condenser have been provided, especially in larger reactors, since about 1970 as auxiliary methods of removing the heat for certain polymers, such as PVC. During the start of a run, the reaction mixture must be heated to the reaction temperatures. Hot water or steam is often used in the jacket for heating purposes.
2. Surfaces that minimize fouling with polymer must be provided. Glasscoated steels were used predominantly until about 1970; the glass surfaces were very smooth, and little polymer collected on them. Unfortunately, resistance to heat transfer across glass coatings is relatively large. Highly polished stainless steel surfaces with almost a mirror

finish are now predominant; such surfaces minimize fouling and are easy to

clean. Figure 9 is a photograph showing the inner electropolished surface of a 15,000 gal reactor. The best heat transfer is realized when lowcarbon steel is clad with a thin layer of stainless steel. Such walls result in almost a 50% reduction in the overall heat transfer resistance compared to glass-coated steels.

3. Vigorous agitation is needed. In larger reactors with a working volume of 40 m³ (or 10,000 gal) or greater, the agitator shaft frequently enters through the bottom of the reactor. More than one impeller is needed in larger reactors.

4. One to four baffles are provided to improve the effectiveness of the agitation. As already mentioned, these baffles are sometimes water cooled.

Suspension polymerization processes are used for about 90% of all PVC produced. In addition, major amounts of polymers are produced using other olefins, including styrene and methyl methacrylate. About 10% of the PVC and some polystyrene are produced by emulsion processes. As already men-

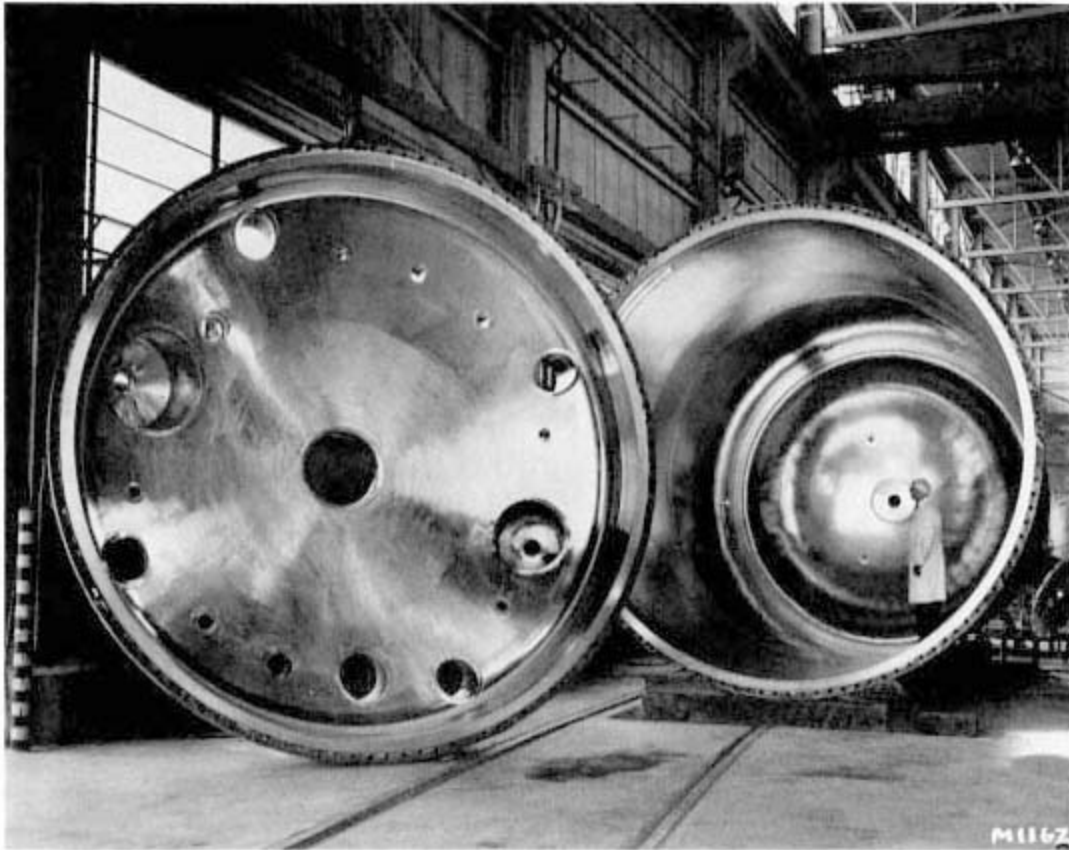


Fig. 9

Inner surface of 15,000 gal reactor that was electropolished by Brighton Corp.
(From Ref. 15 with permission of Krieger Publishing Co.)

tioned, styrene-butadiene elastomers and poly(tetrafluoroethylene) are produced by emulsion polymerization, as are numerous specialty polymers.

PVC Production Using Suspension Polymerization Process [15, 18]

Vinyl chloride is generally polymerized at about 45–70°C producing highly porous particles of PVC that can be easily plasticized. Porous particles absorb or "soak up" the liquid plasticizers readily, and yet they "flow" well in the subsequent extrusion or molding equipment. The PVCs produced in suspension processes are also used in large quantities in rigid or nonplasticized products. The temperature for a specific batch run is selected to a considerable extent to produce the desired molecular weight polymer.

Several significant improvements have been made in the last several years in regard to both the equipment and the operating procedures. These improvements have resulted in improved quality polymers and also in reduced operating costs. Reactors with working volumes in the range of 20,000–52,000 gal (about 80–200 m³) have now been commercialized; up to about 1970, reactors in the 2,000–5,000 gal range (420 m³) were prevalent. Temperature control constraints then limited the size of reactors that could be used. The improvements or modifications that have been made include the following:

1. Reflux condensers and water-cooled baffles were developed in which fouling was greatly reduced. These devices permitted much higher rates of heat transfer as required in larger reactors. Part of the vinyl chloride that refluxes apparently is not mixed well with the initiator and surfactant when it returns to the reactor; that part is thus essentially dedicated to the cooling system for the reactor.
2. Improved materials of construction and improved surfaces for the reactors have been developed to minimize fouling of the surfaces and to obtain higher rates of heat transfer.
3. Certain chemical techniques have also been developed to pretreat the inner reactor surfaces before batch runs. These techniques result in less PVC fouling of the surfaces, higher rates of heat transfer, and easier and less frequent cleaning of the reactor surfaces between runs.
4. Improved jackets have been developed for the outer walls of the reactor. Half-pipe jackets are especially effective in providing high overall heat transfer coefficients. Jackets are also sometimes provided on both the bottom and top heads of the cylindrical reactors.
5. Improved initiators (or combination of initiators) are now available. These improvements include initiators that are more active, that result in more uniform rates of polymerization during a batch run (and hence in shorter times of polymerization), and that minimizes PVC fouling of the walls.

PVC producers can vary the ratio of water to vinyl chloride in a batch run. Higher ratios mean less PVC is produced in a batch run but less heat

must be transferred. Hence, temperature control is easier at high ratios. Based on economic considerations, a ratio of about 1.25 is optimum [25,26]. The type of PVC product and specifically the porosity of the particles is affected by the ratio. Relatively high ratios are sometimes economically justified to obtain special grades of PVC.

PVC reactors often currently operate so that a batch run is completed in 616 h. During such a run, the following occur: loading the reactor with reactants, preheating of reactants, polymerizing the vinyl chloride, emptying the reactor, and cleaning the reactor (as necessary). The time for the polymerization step is sometimes as low as 4 h, but it is often substantially longer, especially with less modern reactors and processes.

The final step in the suspension polymerization process is separation of the unreacted vinyl chloride, water, and surfactant from the solid PVC particles. Most of the vinyl chloride is vaporized from the suspension by reduction of the pressure and by bubbling steam through the suspension for a short period of time. A centrifuge is used to separate most of the water from the PVC particles. The particles are then washed several times with clean water and centrifuged to remove the surfactants or stabilizing agents. Finally, the PVC particles are dried; precautions must be taken not to overheat the PVC, which degrades rather easily.

Computer programs have been developed to estimate the total cost of polymerizing a given amount of vinyl chloride. The lowest production costs are obtained with larger reactors that are operated with relatively fast rates of polymerization [25, 26].

Polystyrene Production Using Suspension Polymerization Processes [14, 15]

Polystyrene processes using suspension polymerization techniques are similar to those producing PVC, but some differences occur, as follows:

1. Heat transfer from the reaction mixture. Reflux condensers are not normally used since styrene is less volatile than vinyl chloride and hence refluxes less readily. Furthermore, considerable styrene would polymerize on the condenser surfaces and would result in poorer quality products. For styrene polymerizations, heat transfer surfaces are apparently always limited to the jacketed surfaces on the walls and to water-cooled baffles. Since the exothermic heat of polymerization for styrene is less on a weight basis, less heat needs to be transferred for a batch run. Reactors as large as 60120 m³ (15,00030,000 gal) have been installed in the last few years. Slightly large ones seem practical [25, 26].
2. Agglomeration of the dispersed organic droplets. Agglomeration is of major concern when 3070% of the styrene has polymerized. At such polymerization levels, the droplets are semiliquid and very sticky. Careful choice of stabilizers is needed to prevent agglomeration.
3. Temperatures and pressures. Temperatures for polystyrene production are often in the

range of 90115°C. Even though temperatures are

considerably higher than for PVC production, the pressures in the reactor are much lower since the vapor pressure of styrene is much lower than that of vinyl chloride. An inert gas is often used as a blanketing agent in the polystyrene reactors to ensure a positive pressure at all times and to prevent air leaks into the system.

4. Higher polymerization levels often result when polystyrene is produced; the levels often approach 100% whereas 90% levels or less are prevalent in PVC units.

Upon completion of a polystyrene run, the suspension is cooled to 60°C (140°F) or less to be below the heat distortion temperature of polystyrene. Agglomeration of polystyrene particles is then minimized. Centrifuging, water washing, and drying are used to recover the final product.

PVC Production Using Emulsion Polymerization Processes [15, 18]

The PVC particles produced by emulsion processes are generally less porous (having higher bulk densities) and are much smaller than those formed by suspension processes. The surfactants employed during emulsion polymerization are mostly retained on the particles. The PVC produced is sometimes used in emulsions or slurries with either water or an organic liquid; these specific emulsions are referred to as plastisols or organosols, respectively. They can be used to coat various solid surfaces with PVC.

Smaller batch reactors are normally used for emulsion processes compared to suspension processes. The heat transfer surfaces on the jacketed walls are generally sufficient to maintain temperature control.

Separation of the PVC granules from the emulsion is relatively expensive. The particles are so small and so well stabilized with surfactants (or emulsifying agents) that centrifuging or filtration is generally impractical. Spray drying is a common method of separation, and considerable energy is required to vaporize the large amounts of water present. Most of the surfactant is retained on the PVC particles.

Modified emulsion processes have been developed in which the emulsion is seeded with tiny polymer particles. As polymerization proceeds, these particles grow in size. Such a technique results in PVC particles that are larger in size than those in which polymerization starts in the micelles.

A continuous-flow process for the production of PVC by emulsion polymerization techniques has been used in West Germany since the 1930s. Reactors with height-diameter ratios of at least three and with internal volumes of at least 5 m³ are used. The feed streams enter at the bottom of the reactor, which requires high levels of agitation. More emulsifiers are usually required in this process to prevent PVC buildup on the inner walls.

Costs of Polymerization

Feedstock costs generally account for well over half of the total production costs. During most of the 1970s, feedstock costs increased sharply, but they then decreased in the early 1980s. After leveling in the middle of the decade, they rose again in the late 1980s. Other production costs are for the following operations: polymerization; separation and recovery of the polymer from the reaction mixture; preparation of polymer for sale, which may include pelletizing or other prefabrication steps, and incorporating additives (e.g., dyes, pigment, stabilizer, antioxidation); and recycling the unreacted feedstocks. These costs vary, of course, with the high polymer being produced and with the specific plant, but they frequently total several cents per pound of polymer produced.

As plant size increases, production costs tend to decrease when expressed as cents per unit weight of polymer produced. There is consequently a trend to build larger plants. Plants for the production of LDPE, LLDPE, HDPE, PP, PVC, and polystyrene are large and sometimes have production capacities of 0.5 billion pounds or more per year, about 250,000 tons or more per year. These specific polymers all have large sales per year [27], but plants for polymers with smaller demands generally have smaller capacities.

Synthetic high polymers were produced to only a limited extent in the nineteenth century, and the major advances in production occurred in the twentieth century. In 1988, more than 46 billion lb plastics were produced in the United States [27]. For the 5 year period from 1983 through 1988, there was in this country a growth rate for plastic production of approximately 63%. There is a consensus that considerable growth will continue for the foreseeable future.

The growth rate for plastic production expressed on a percentage basis has been even larger in some nations, especially in developing ones. High polymers continue to replace metals, glass, paper, wood, and so on in many applications. This replacement has occurred primarily because of reduced costs and improved properties of several plastics. Two examples are as follows: LLDPE, introduced in the late 1970s, has a much higher tensile strength than the LDPE that was previously available. Production costs for LLDPE are in addition generally also less. Second, a polyethylene product was announced in the 1980s that has a tensile strength greater than that of steel; this product can be used in bulletproof shields. It is, however, quite expensive to produce.

The annual production rates of synthetic fibers and of synthetic rubbers were by 1988 about 9.1 and 5.13 billion lb, respectively [27]. Major technical improvements have occurred in the recent past in these two industries as well as the plastics industry, and further improvements seen imminent. These improvements and/or the increased demand for specific high polymers are necessitating new plants and/or modernization or enlargement of older plants.

Most polymer plants produce at least several types of a given high poly-

mer. Each type has somewhat different properties and different markets (or end uses). These types are produced by varying the operating conditions, with the result that some of the following molecular features vary: average molecular weight, spread of molecular weights, branching, stereospecificity, and others. In designing such a plant, provisions must be made to permit adequate variations in operating conditions. In the case of PVC, production costs for these different types of products often vary by 0.10.5 cents/lb [25, 26].

Alternative processes are available for the production of all major high polymers. These processes have at least slightly different operating costs and also invariably produce polymers with somewhat different properties (and molecular structures). In selecting a process, a company needs to consider both the production costs and the market.

Conclusions and Summary

A specific polymer (or copolymer) can be and is often produced commercially by very different processes or at least very different types of reactors. LDPE, LLDPE, HDPE, PP, polystyrene, PVC, styrene-butadiene elastomers, poly(ethylene terephthalate), and nylon are the examples considered here. Alternative polymerization methods result in somewhat different molecular structures and properties of a given polymer; production costs also vary. Polymers produced by certain processes are, however, often preferred for specific uses.

Recommended Additional Reading

More details on processes for polyethylene, polypropylene, PVC, polystyrene and ABS are reported by Albright, *Processes for Major Addition-Type Plastics and Monomers*. 2nd ed., Krieger, Malabar, FL, 1985.

General material on polymerization mechanisms, are included in Billmeyer, *Textbook of Polymer Science*, 3rd ed., Wiley-Interscience, New York, 1984.

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Polymerization, Emulsion

Louis R. Roberts

Introduction

Emulsion polymerization is one of several processes by which a variety of unsaturated organic carbon compounds can be polymerized. This polymerization, which is an addition type, is carried out in liquid medium, almost always aqueous, and produces a milky fluid called a latex.

There are four basic ingredients required for an emulsion polymerization. These are (1) the monomer, (2) the dispersion medium, (3) an emulsifier, and (4) an initiator. When correct amounts of the ingredients are mixed together properly in a suitable container within a certain temperature range an emulsion of monomer droplets is formed in the continuous dispersion medium. The initiator causes the monomer molecules to polymerize. When the polymerization is complete, a stable emulsion of polymer particles will remain.

Organic monomers commonly polymerized using this process include acrylic and methacrylic acid and especially organic esters such as methyl and ethyl acrylates and methacrylates. Acrylonitrile, butadiene, and styrene are very important monomers because of their use in making rubbers. It is quite common to produce polymers using more than one monomeric substance.

It is possible to carry out emulsion polymerization in media other than water, but there is no publicly known practical application of the use of any medium other than water. It must be noted, however, that the presence of water-soluble organic chemicals such as methanol or acetone in the emulsion polymerization recipe frequently facilitates the process and improves the properties of the product.

The emulsifier may be comprised of a wide variety of surface-active agents or soaps. These materials solubilize the monomer to a certain extent, enable the formation of the emulsion of the organic monomer phase and the water phase, and then perform a stabilizing function in the polymer-water emulsion product.

It is now generally accepted that emulsion polymerization occurs almost entirely following the radical mechanism. The function of the initiator is to cause the formation of the radicals, which in turn lead to the propagation of the polymer molecules.

Other substances may be included in the recipe of an emulsion polymerization process. However, any substance so included will be only to enhance or supplement the function of the four materials listed above.

A typical recipe for an emulsion polymerization is as follows:

Constituent	Parts by Weight
Monomer	100
Dispersing medium (water)	150
Micelle generator (soap)	5
Initiator	0.5

Some general characteristics of emulsion polymerizations should be recognized. One is that this is an addition polymerization. Assuming a water medium, another characteristic is that the active centers and propagation loci are located in the water phase. Blackley, in his excellent book [2], lists two definitions of emulsion polymerization:

1. An addition polymerization process in which the several concurrent propagating centers are isolated from each other.
2. An addition polymerization process which proceeds by micellar mechanism.

An important observation concerns the difference between suspension and emulsion polymerization. In the former the polymerization occurs in the organic or monomer phase, while in the latter it occurs in the water phase or medium.

The main advantages of the emulsion polymerization technique are: (1) the water provides an excellent heat sink, so that the heat released by the polymerization reaction can be adequately dissipated; (2) polymers of high molecular weight can be formed at a rapid rate; and (3) the molecular weight and degree of polymerization can be easily controlled so that a product having specific and reproducible properties can be obtained.

One serious disadvantage is the necessity for separation if the polymer is desired in a solid form. In many cases the product desired is the latex in which case there is no disadvantage, but when a solid product is desired the coagulation and recovery of the solid polymer is a multistep operation requiring additional materials and equipment.

Other disadvantages include (1) the presence of the emulsifier and possibly other constituents if a pure polymer is desired, and (2) the requirement for larger or multiple operating equipment needed for the same polymer production rate, since the polymer comprises usually less than 40% of the bulk of the reaction system.

History

Hohenstein and Mark [16] indicate that bulk polymerizations were carried out as early as 1835. The earliest references to emulsion polymerizations are found in the period of 1909-1915 [7, 15]. Referring to the definitions given above, there is some doubt that this early work actually involved emulsion polymerization. The work of Dinsmore [5] and of Luther and Heuck [18] seem quite clearly to be true emulsion polymerizations. Recipes are given in the latter publication.

Whitby and Katz [27] list the additives that characteristically lead to an emulsion polymerization.

Hohenstein and Mark [16] quite clearly and correctly differentiate among the processes we term as solution, suspension, and emulsion polymerizations.

Applications

As indicated earlier, the emulsion polymerization process is used to polymerize a variety of unsaturated organic monomers. Notable among these are the alkyl acrylates, alone and in conjunction with other monomers such as acrylic and methacrylic acids. Olefins and vinyl esters of carboxylic acids are also polymerized alone and with other monomers in emulsions.

Acrylonitrile, butadiene, and styrene are used extensively to produce rubbers of a wide variety of properties which are influenced by the relative quantities of the copolymer constituents.

Besides rubbers and elastomers, the more common applications for emulsion polymers include paints and other coatings, binders, adhesives, and polishes.

Specialty products such as stain and water repellents can be produced by making certain chemical substitutions in the molecules of the monomer.

Process Theory

General

We are indebted to Harkins [912] for his notes on the qualitative theory concerning the mechanisms involved in emulsion polymerization. Many other scientists have made significant contributions to our understanding of the process. It is beyond the scope of this work to try to list them all. Blackley [2] does an excellent job of listing these contributions.

A simplified outline of the process will be presented first, with a more detailed account of the various steps of the process following. Figure 1 gives a

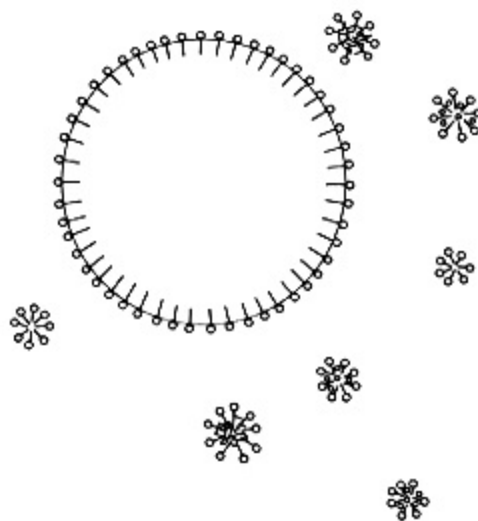


Fig. 1.
Soap molecules at micelle interface.

graphic illustration of the reaction system. The water phase contains the species represented. Mechanical agitation breaks the monomer phase into small droplets. The droplets are held in suspension by the action of the agitation and of the emulsifier molecules, the hydrophobic portions of which are absorbed into the monomer droplets. The hydrophilic portion of the emulsifier molecules remain in the water phase.

In many cases, although not in all, the monomer is only slightly soluble in water. In all cases, but particularly in the cases in which the monomer is only slightly soluble in water, the emulsifier or soap solubilizes the monomer in the water, or, in other words, causes or enables more monomer molecules to be dissolved in the water phase. This action is attributed to the formation of micelles which are tiny groups of perhaps 50 to 100 soap molecules [8] clumped together with their hydrophobic portions adjacent to each other and the hydrophilic portions adjacent to each other and also in more intimate contact with the water. This juxtaposition of the soap molecules results in the formation of a tiny particle called a micelle in which there is a largely hydrophobic region that tends to attract the organic monomer molecules. Bovey, Kolthoff, Medalia, and Meehan list calculated molecular weights of micelles of various surface-active agents on page 154 of their excellent book [3].

With the emulsion of the monomer phase in the water established, and the presence of the micelles comprised of soap molecules and solubilize monomer molecules presumed, the initiator is added. The initiator is chosen for its propensity to break down into charged radicals. These radicals in turn react to form new radicals from the monomer molecules. These new radicals then combine with other monomer molecules following the addition polymerization procedure.

One of the basic characteristics of emulsion polymerization is that the polymerization occurs in the water phase and not in the monomer or organic phase. This indeed is the primary difference between emulsion and suspension polymerization. Since the majority of the monomer molecules dissolved in the water phase are located within the micelles, most of the polymer molecules are initiated in the micelles. There are, no doubt, comparatively few initiations that occur in the true aqueous phase, outside of the micelles.

The next step of polymerization is propagation. As the monomer molecules in the micelles combine with one another, more will migrate from the droplets through the water to the micelles. Thus the micelles grow from tiny groups of soap and monomer molecules to larger groups of polymer molecules, held in emulsion by the action of the soap molecules located on the exterior surface of the particle. With time, all of the micelles disappear and the monomer droplets shrink in size. The end of the process is that point in time when all of the monomer molecules in the droplets are transferred to the polymer particles, and essentially all of the soap molecules are also attached to the polymer particles.

Emulsification

It would appear to be obvious from the foregoing that a successful emulsion polymerization process requires an acceptable emulsification system. As indicated earlier, an acceptable emulsification results from a combination of

optimum agitation and the correct amount of the proper emulsifying agent or soap.

For many polymerization systems a satisfactory degree of agitation includes a wide range of agitator speeds. However, some systems are more sensitive to agitation, and greater care must be exercised in determining the optimum agitator speed for the specific liquids being handled and the specific mechanical equipment being used.

In general, the agitator speed must be high enough to break up the monomer phase into droplets, but not so high as to create so much shear that the emulsified polymer particles in the product are mechanically coagulated. No doubt many experimenters have viewed with dismay the slimy mess created when polymerization occurs in a vessel in which the agitator speed was too low to break up the monomer phase into droplets. On the other hand, too high an agitator speed results in an excessive coagulum formation adhering tenaciously to the surfaces of baffles, agitator impellers, and vessel walls. The coagulum formation represents a loss in yield.

The emulsifying agent or soap has a multirole function to play in the emulsion polymerization process. First of all, the soap must form the micelles which solubilize the monomer and within which the initiation and early propagation of the polymer particles occur. The soap also helps emulsify the monomer and then stabilizes the emulsified polymer particles as they grow and also in the final product.

A large number of materials can be used as the emulsifying agent. These materials are generally classified as either anionic, cationic, or nonionic. By far the greatest number of emulsion polymerizations are carried out using an anionic soap. Anionic soaps often used include carboxylates, sulfonates, and sulfates. Rosin acids and other types can also be used.

Cationic soaps are ordinarily used only in special situations. The anionic soap systems seem to be less subject to disturbances by minor changes in the other process variables. Thus they are more reliable in the sense of confidence of trouble-free operations. However, in special situations, such as when an anionic system would be repelled by a surface to which it is to be applied, cationic systems are useful. Cetyltrimethylammoniumbromide is probably the most commonly used cationic emulsifier. Many other compounds of a similar nature are referred to in the literature.

Nonionic emulsifiers are also used, most generally when ionic ones are not applicable for some special reason. One special advantage of this type of soap is that the latex is insensitive to a wide range of pH. The structures of these soaps commonly include a long-chain alkyl group attached through an oxygen or nitrogen atom to a chain of ethylene or propylene oxide groups. Helin and coworkers [13] have considerable data concerning the performance of this type of emulsifier.

Of immediate interest is the quantity of soap to be used. Earlier a typical recipe was listed and other more detailed recipes will be given later. The criterion for specifying the

quantity of soap is that there must be sufficient soap present so that the critical micelle concentration is exceeded. Shinoda [22] and Harkins [11] give critical micelle concentrations for various long-chain carboxylates and alkylbenzene-sulfonates as well as other types of emulsifiers.

The critical micelle concentration concept comes from the observation that

the surface free energy at the air-water interface of a dilute soap solution decreases to a certain point as the concentration of the soap increases. Beyond that point the surface free energy remains constant as additional soap is added. The theory is that the soap molecules align themselves at the interface until that is saturated and the additional soap molecules form the micelles as represented in Fig. 1.

The work of Shinoda [22] resulted in the development of the equation

$$\log_{10} (\text{CMC}) = ABn$$

where CMC stands for critical micelle concentration in moles per liter. The value for A proved to be close to 1.70 for most anionic and cationic soaps investigated, while the value of B was close to 0.292. n is the number of carbon atoms in the hydrocarbon chain of the molecule.

Since the critical micelle concentration can be estimated, the question becomes how much soap should be included in the recipe? The answer is that successful polymerizations have been carried out wherein the soap concentration was 10 times the critical micelle concentration. This concentration is lower than appears to be normal, however. A good round number might be that sufficient soap should be used to exceed the critical micelle concentration by a factor of 50 to 100. A practical approach to establishing a recipe will be discussed later.

It should be noted at this point that the quantity of soap present in the system affects not only the rate of polymerization but also the number and size of the polymer particles. The Smith-Ewart theory [24] and other quantitative treatments will be addressed later. The optimum quantity of soap is definitely influenced by whether a fine or coarse grain product is desired. In other words, if a product is desired that has a large number of relatively small particles, a relatively large amount of emulsifier should be used. Conversely, if the product should have a small number of large particles, less soap must be used.

Initiation

To begin with, the initiator must be a substance that will generate an active radical in the emulsified water-monomer system. Once the initiator generates a radical, the radical may be transferred to the propagating loci in more than one procedure. The initiator radical may react with other molecules in the water phase, including the water molecules, to create a different radical. It may also react with a monomer molecule that is dissolved in the true water phase to create an active monomer radical. Or the initiator radical may enter a micelle where it reacts with a monomer molecule to create an active monomer radical.

Directly or indirectly the initiator creates a propagating center in the micelles since the activated species that survive are absorbed into the micelles. Once the propagation proceeds far enough, the micelles are no longer that but polymer particles instead.

Initiators are generally divided into two broad classesnamely, dissociative and redox. Possibly the most common initiator, potassium persulfate

(K₂S₂O₈), will function in either classification. It will dissociate thermally to form the active sulfate radical ($\text{SO}_4^{\cdot -}$), and may be reduced by a bisulfite salt to give the same radical while another radical ($\text{HSO}_3^{\cdot -}$) is also formed.

Actually the persulfate salt is by far the most common dissociative initiator. Others used include aromatic diazoamino compounds, aromatic diazothio ethers, and alkali metal aryl diazoates.

Redox systems commonly used include persulfate-mercaptan systems, persulfate-bisulfite systems, chlorate-bisulfite systems, hydrogen peroxide-iron(III) salts, hydroperoxide-iron(II) salts, and other less common systems.

Smith [23] demonstrates that, provided the number of reaction loci is fixed, variation in the quantity of initiator has no effect on the rate of polymerization. However, it has been noted that the use of a redox initiator usually results in a significantly increased rate of polymerization. This is attributed to the sudden influx of a high concentration of radicals, thus causing the creation of new loci of propagation. The Smith-Ewart [24] theory accounts for this phenomenon.

The real value of the redox system is that the polymerization can proceed at a higher rate at significantly lower temperatures compared to the temperatures required for the dissociative systems to proceed satisfactorily.

The recipes given in a following section should give an adequate idea for the quantities of initiator to use, or at least to a first approximation.

A detailed discussion of the mechanism of initiation does not seem pertinent to this work. Blackley [2] includes a lengthy discussion. Bacon [1] presents a comprehensive review concerning redox systems.

Quantitative Theories

Smith-Ewart Theory

Basing their deliberations on Harkins' theory [912], Smith and Ewart [24] developed an expression for the rate of polymerization in an emulsified system such as has been described. These workers considered different situations, but for the optimum polymerizing conditions arrived at the result that

$$dM/dt = \frac{1}{2} k_p [M] N$$

where N is the number of loci per unit volume of aqueous phase, M is the molal concentration of the monomer at the polymerization locus, and k_p is the rate coefficient for the propagation step. In these terms dM/dt gives the rate of conversion of monomer to polymer in number of monomer molecules converted per second in a unit volume of aqueous phase. This expression holds only for that period during which the number of

polymerization loci has reached its maximum and before the monomer droplets disappear. Presuming the Harkins theory to be valid, the Smith-Ewart work leads to the conclusion that the rate of polymerization during this period is of the order of 0.4 with

respect to the beginning initiator concentration and of the order of 0.6 with respect to the concentration of the emulsifier.

Gardon's Theory

A number of investigators have made refinements of the Smith-Ewart work [20, 21, 25, 26]. However, Gardon, in a series of articles [6], has enlarged on the Smith-Ewart theory, producing an equation with which to calculate the number of particles produced in a polymerization. This in turn leads to the size of the polymer particles in the latex. Further, Gardon worked out a conversion-time relationship, how the size of the polymer particles and the molecular weight of the polymer change with degree of conversion, and the effect of emulsifier, initiator, and the status of the monomer supply in the reacting system. Gardon's treatment is consistent with the Harkins theory.

Gardon divides the emulsion polymerization into three stages. During the first period new polymer particles are being formed. In the second stage no new particles are being formed, but monomer still exists in droplets. In the third stage the monomer droplets have disappeared and the polymerization is proceeding in the particles formed during the first stage. It was necessary to have these three stages in order to allow for a mathematical treatment of the reaction system.

Gardon's equation for the number of polymer particles formed is

$$N = 0.208 A^{3/5} R^{2/5} K^{-2/5}$$

where A is the total interfacial area of polymer particles and micelles together per unit volume of aqueous phase, R is the rate of production of effective radicals per unit volume of aqueous phase, and K is the rate of increase of the cube of the radius of the polymer particles:

$$K = \frac{d(r^3)}{dt} = \frac{k_p}{4\pi N_A} \frac{\rho_m}{\rho_p} \frac{v}{1-v}$$

where k_p is the rate coefficient for the propagation, N_A is Avogadro's number, ρ_m and ρ_p are the densities of the monomer and polymer, respectively, and v is the volume fraction of the monomer in the polymer particle.

Experiments have shown excellent agreement between actual values and those predicted by Gardon's equations.

Production

In the Introduction a typical recipe for an emulsion polymerization was given. This was a highly simplified recipe showing relative amounts of the basic ingredients in an emulsion polymerization. In commercial practice the recipe

becomes more specialized and detailed. As indicated in the Process Theory section, the relative quantities of the components of the recipe are varied in order to produce the polymer having the desired properties.

In an excellent monograph Emulsion Polymerization of Acrylic Monomers the Rohm and Haas Co. presents recipes for producing several different polymers of acrylates by themselves and in copolymerizations with different combinations of a number of other acrylates. The effects of using different combinations of initiators and emulsifiers are indicated.

The effect of the presence of different amounts of inhibitor is also shown. Commercially available acrylates will almost surely contain an inhibitor to prevent autopolymerization of the material. Methyl ether of hydroquinone (MEHQ) is possibly the most commonly used inhibitor. During the production of the desired polymer, the action of the inhibitor must be overcome by the presence of a sufficient quantity of a radical generating material.

In one case the following recipe is used:

376 ml dionized water
 24 g emulsifier
 200 g ethyl acrylate
 4 ml ferrous sulfate solution (0.3 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 200 ml water)
 1 g ammonium persulfate
 1 g sodium bisulfite
 5 drops t-butyl hydroperoxide (70%)

The water and emulsifier are placed in the reaction vessel, which is then purged of air by using nitrogen. The monomer, ferrous sulfate, and the persulfate are added and stirring is continued for 1530 min. The temperature is controlled to 20°C. Then the bisulfite and hydroperoxide are added. Polymerization begins immediately in the case of uninhibited monomer, as evidenced by a sharp temperature rise. When a monomer inhibited by 200 ppm MEHQ is used, an induction period of 8 min is observed. A substantial difference in the size of the polymer particles is also observed, with nearly 40% larger particles noted in the case of the inhibited monomer. The polymerization goes to essential completion in 15 min after the start of the temperature rise.

The need for purging the reaction vessel of air must be emphasized. Oxygen has been found to be a serious inhibitor of the polymerization process and must be effectively eliminated from the system. Practice has shown that reaction vessels may be "poisoned" by contaminants that prevent polymerization from occurring. Some producers have found that conditioning a cleaned reaction vessel system is useful. This is accomplished by charging the vessels with all of the reaction constituents except the monomer and agitating these materials for a period of time at temperatures to be expected during the polymerization process.

Figure 2 shows typical mechanical equipment that can be used for the commercial production of emulsion polymers. In this case a mixing vessel is used in which the emulsion is prepared. This is then transferred at the desired temperature to the reaction vessel where the initiator is added and the polymerization occurs. Finally the product is transferred to a receiver where

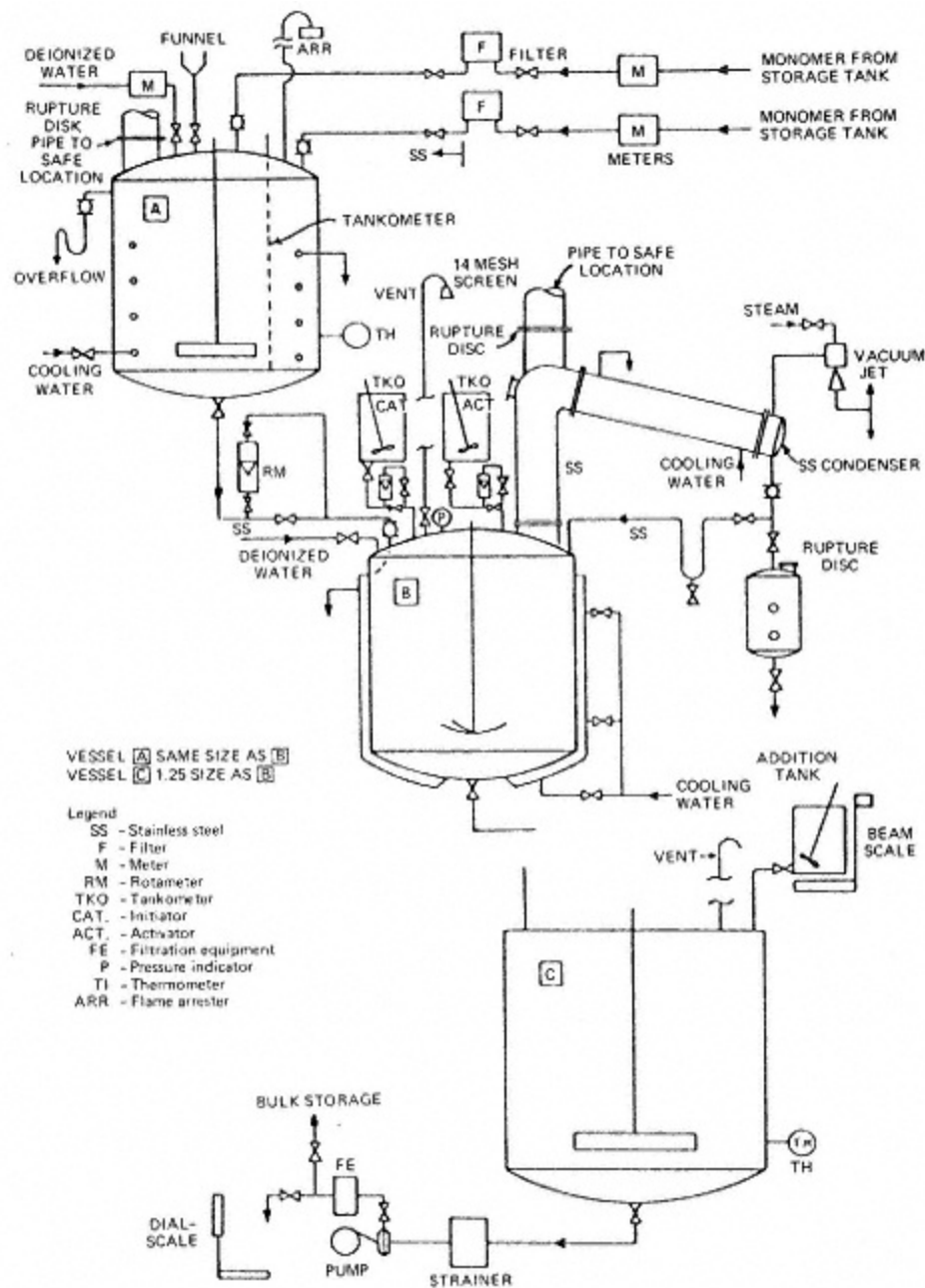


Fig. 2.
Plant for emulsion polymerization.

adjustments may be made to product concentrations or where desired additives can be blended in.

This system may be operated in either the batch or the continuous mode. By using the batch type of operation a polymer with a narrower range of molecular weight will be produced, compared to that produced from a continuous

operation. Care must be taken, especially during the batch operation, to exclude air from the system. Periodic reactor cleaning operations are necessary in either case, since the presence of excessive quantities of coagulum in the vessel may interfere with operations and with product quality.

It should not be expected that one will be able to produce an emulsion polymer with the desired properties without considerable experimentation. The information included so far in this article can be used to establish a first approximation formulation. Also, one should be able to discern what formulation changes to make in order to achieve necessary changes in properties.

A highly recommended statistical procedure by which the property characteristics of the polymer can be optimized with a minimum of experimental effort can be found in a series of articles [4, 14, 17]. Laboratory experimentation can establish the extent of the effect of specific increments of changes in certain operating variables such as concentrations of ingredients and impeller speed.

The statistical treatment will indicate the number of experiments to run and the values of the variables to use in each experiment. The approximate optimum value of the variables should be indicated at the end of the exercise. If confirmatory runs do not produce the material with the desired properties, the direction and extent of needed changes in the operating variables can be deduced from the statistical treatment.

Further, if scale-up to pilot plant and commercial production levels does not result in a product of the same desired properties, again the direction and extent of needed adjustments will be known.

The extent to which refinements to the basic procedure described in earlier sections are practiced is illustrated in the following description of the production of styrene-butadiene rubber (SBR) compiled by B. F. Goodrich Chemical Co. personnel from the literature to avoid any conflict with proprietary information.

SBR can be produced at temperatures of 50°C (hot rubber) or 5°C (cold rubber). The cold rubber exhibits properties considered to be superior to those of hot rubber. A typical formulation in parts by weight for cold rubber is [19]:

Butadiene	71.0
Styrene	29.0
tert-Dodecyl mercaptan	0.18
p-Menthane hydroperoxide	0.08
Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	0.03
Trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot$	

10H ₂ O)	0.5
Tetrasodium salt of ethylenediamine-tetracetic acid (EDTA)	0.035
Sodium formaldehyde sulfoxylate	0.08
Resin acid soap	4.5
Water	200.0
Hydroquinone	0.01
Temperature	5 °C
% Conversion	60
Reaction time	12 h

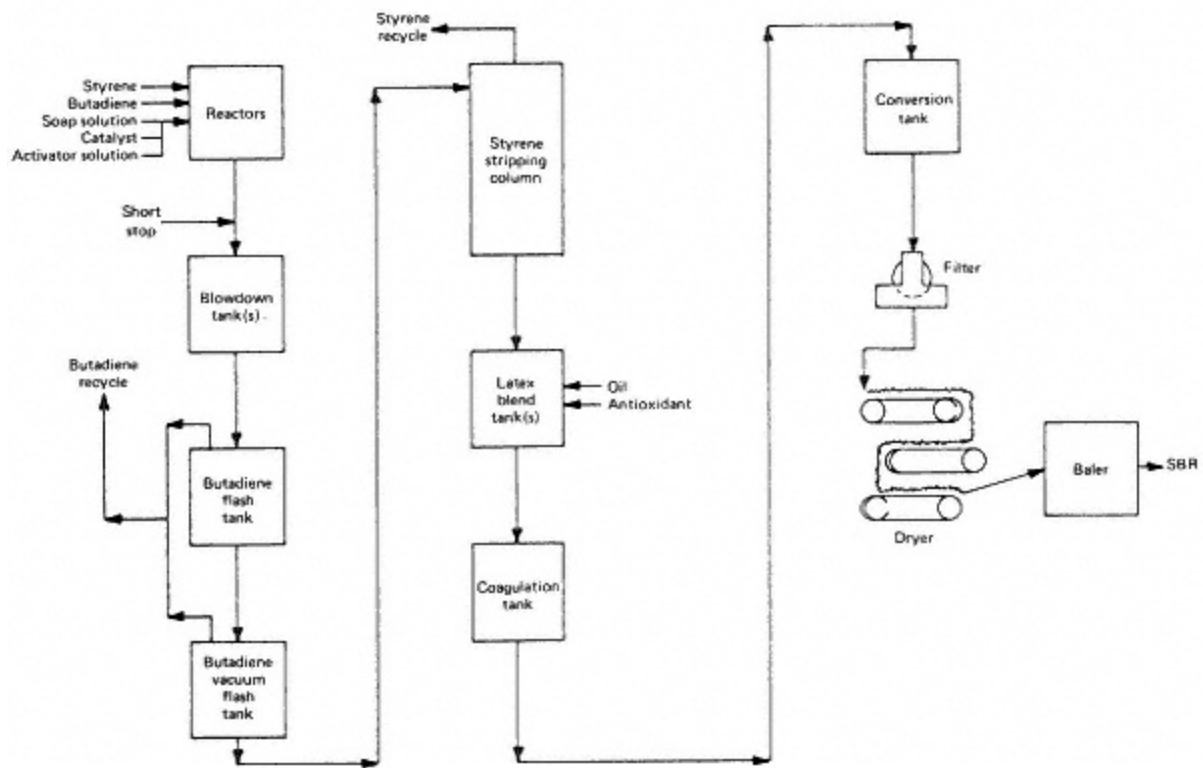


Fig. 3.

Typical flow sheet for the production of styrene-butadiene rubber.

[Source: The Vanderbilt Rubber Handbook, G. G. Winspear (ed.), Vanderbilt, New York, 1968, p. 39.]

This is a batch process. The solution of the ferrous sulfate chelated with the EDTA and sodium formaldehyde sulfoxylate is included in the soap solution. The hydroperoxide is dissolved in a portion of the styrene for charging after the other ingredients have been mixed and cooled to reaction temperature. This mixture constitutes the initiator system. Usually a 50:50 mixture of fatty acid and rosin acid is used in this recipe to increase the soap solution's fluidity and to enhance the building tack of the rubber.

The function of the soap as emulsifier has been described earlier. In this case a secondary emulsifier such as a sodium alkyl aryl sulfonate is used to reduce the amount of solid rubber that falls out of the emulsified product and deposits in the vessels, pipes, and pumps. Deposition of coagulum is a severe problem in the production of SBR.

The mercaptan compound is used to control the molecular weight of the polymer by reducing cross-linking. The mercaptan serves as a chain transfer agent.

The sulfoxylate initiator system is preferred in the cold polymerization process because of its high activity and the fact that it does not cause discoloration in the product. The system uses hydroperoxide as the oxidizing agent, sodium formaldehyde sulfoxylate as the reducing agent, a sequestering agent, and trace quantities of iron(III) in the form of ferrous sulfate.

In order to counteract the inhibiting action of any oxygen present, a reducing agent such as sodium hydrosulfite could be added to the soap solution. An electrolyte such as trisodium phosphate or potassium chloride is added to buffer the emulsion system. This stabilizes the emulsion against changes in pH, and the electrolyte also reduces the viscosity of the reaction mixture, thereby improving agitation and heat transfer.

Referring to Fig. 3, the butadiene, styrene, soap solution, initiator system, and part of the charge water are added to the first vessel, the reactor. Assuming a batch operation, the reaction is stopped at the desired conversion, which is about 60% for cold rubber. The percent conversion can be followed by sampling and determining the percent solids in the latex. When enough experience is gained in the operation, percent conversion should be closely approximated as a function of reaction time. The reaction is stopped by the addition of a shortstop agent such as hydroquinone.

The latex is then transferred through a series of vessels where the unpolymerized butadiene is flashed and stripped from the latex, and the unpolymerized styrene is subsequently stripped out. A rubber anti-oxidant such as N-phenyl-B-naphthylamine is added. The latex is then coagulated by the addition of brine, followed with dilute sulfuric acid or aluminum sulfate. The coagulated crumb is washed, dried, and baled.

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Polysilicon Processes, Economics

Carl L. Yaws
and Jack R. Hopper

Introduction

The modern-day electronics industry, which includes televisions, radios, electrical appliances, automobile components, calculators, and personal computers, would not exist without semiconductor-grade polysilicon. These modern conveniences, which enhance the quality of life for humanity, will increase to even larger usage in the future. This article focuses on the economics of producing polysilicon for the electronics industry. The results are intended to be semiquantitative and useful in initial project studies.

Two processes are covered. The first is the Siemens process, which uses trichlorosilane (SiHCl_3 , TCS) as the silicon source material for producing polysilicon. This is the process used by most companies in the United States, Japan, and Europe to produce semiconductor-grade polysilicon. This includes the major producers, such as Hemlock Semiconductor (United States), Monsanto (United States), and Wacker (Europe). The second pro-

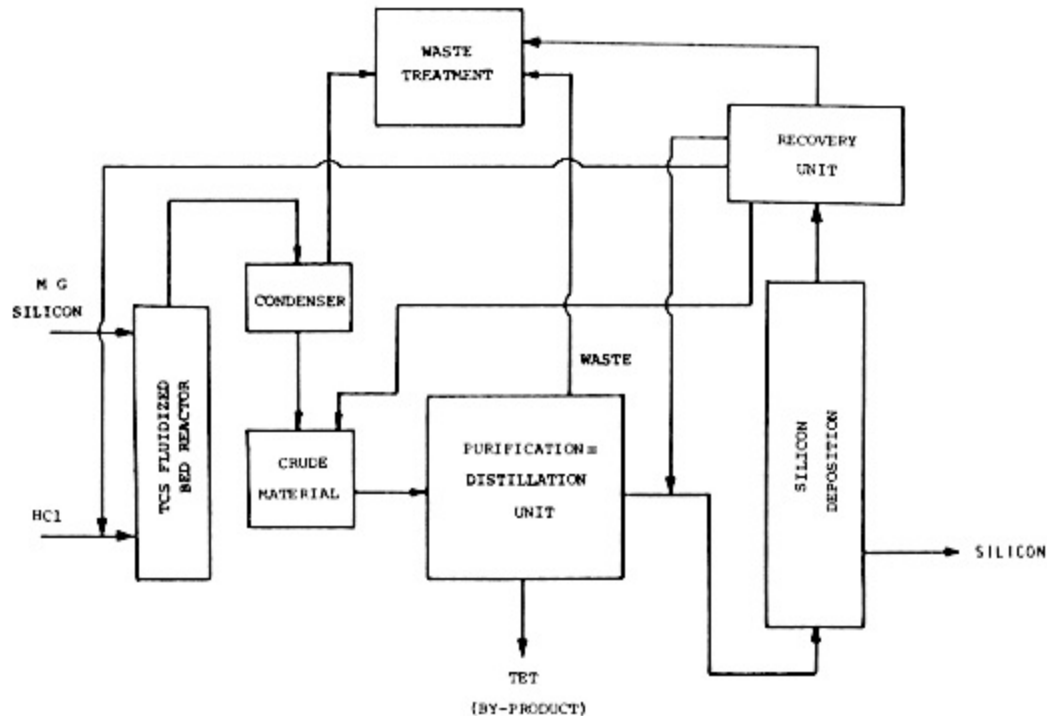


Fig. 1
Siemens process.

cess is referred to as the Union Carbide process. This process uses silane as the silicon source material for producing polysilicon. This process is used by Union Carbide in the United States and Komatsu in Japan.

The economics of producing polysilicon by fluidized bed technology are not discussed. At the present time, most of the polysilicon produced in the United States, Japan, and Europe is not achieved by fluidized bed technology. Most of the polysilicon is produced by silicon deposition on the surface of a hot rod.

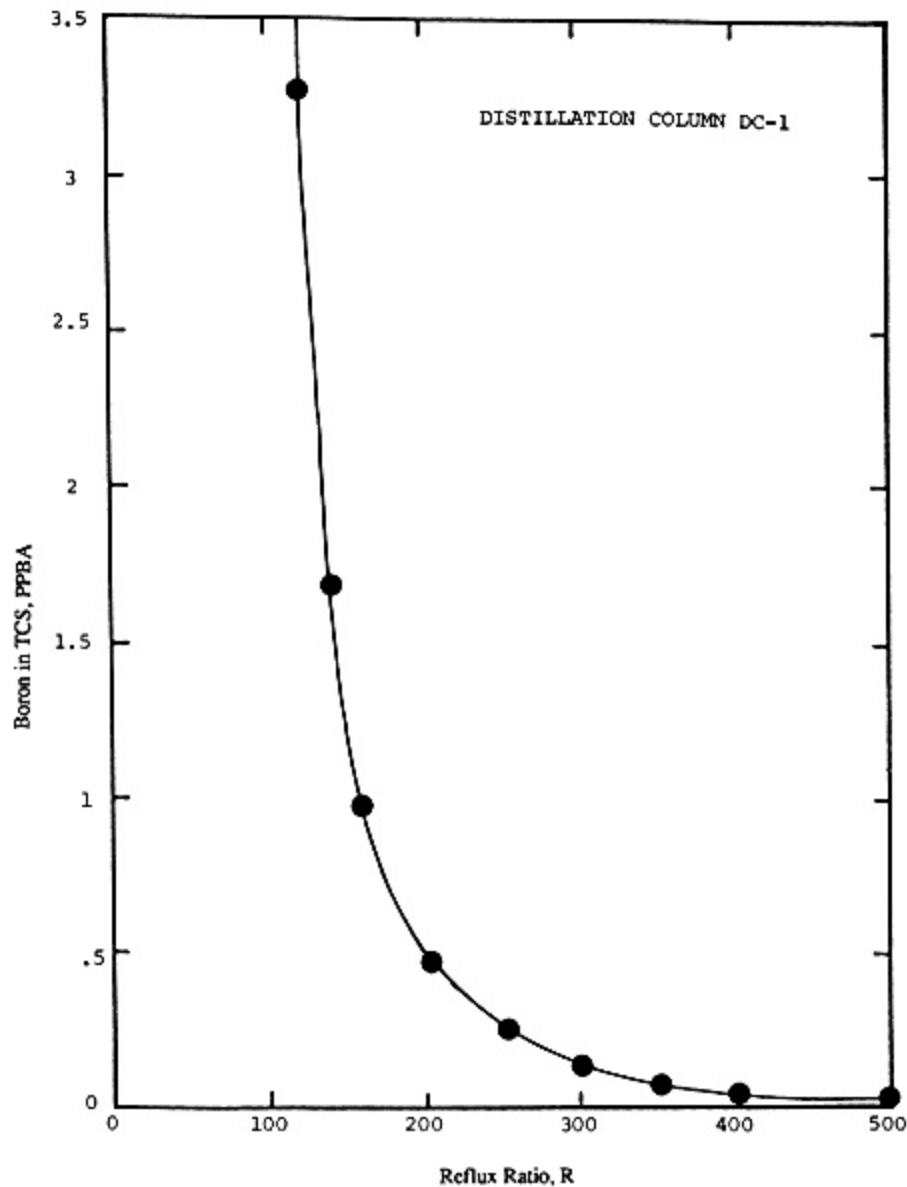


Fig. 2
Representative results for boron impurity removal.

Siemens Process

Process Description and Design

The flowsheet for producing polysilicon by the Siemens process is shown in Fig. 1. Initially, metallurgical-grade silicon (MGSi) is reacted with anhydrous hydrogen chloride (HCl) in a fluidized bed reactor (300-350°C) to produce a mixture of chlorosilanes. The mixture is primarily trichlorosilane

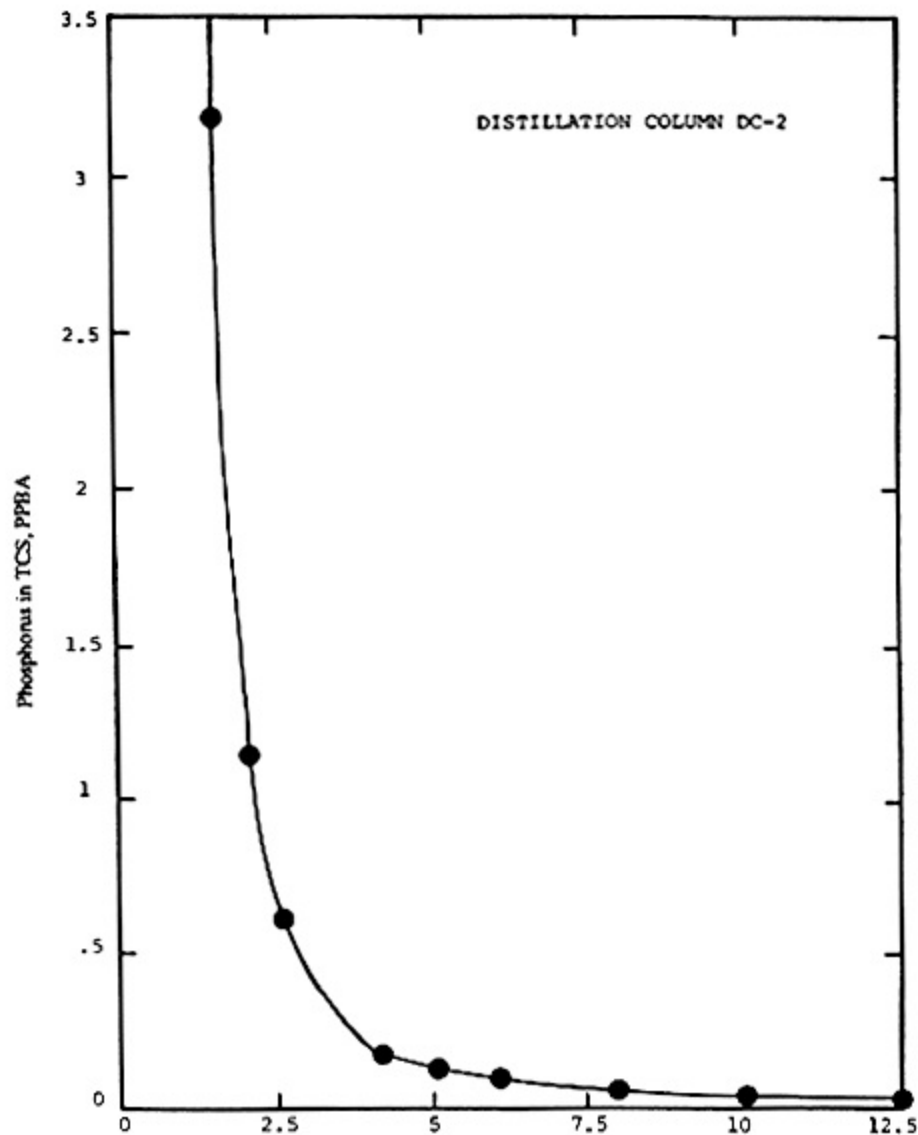
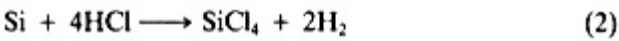
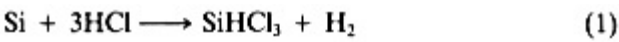


Fig. 3
Representative results for phosphorus impurity removal.

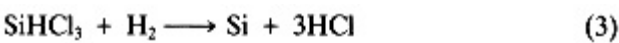
and silicon tetrachloride (TET), which are produced via the representative reactions



Since the reactions are highly exothermic, heat transfer for the removal of the heat of reaction is required to maintain reaction temperature control.

The mixture of chlorosilanes from the reaction is condensed and subjected to several distillations to separate by-products and remove impurities. Representative results for boron impurity removal from TCS are shown in Fig. 2. Figure 3 presents representative results for phosphorus impurity removal. The TCS issuing from the distillation is extremely pure, with only parts per billion (ppb) of electrically active impurities in the silicon source material.

The purified TCS is reacted with hydrogen (H2) in a hot rod reactor to produce polysilicon deposition via the representative reaction



The deposition reaction occurs on the surface of a hot rod (1,0001,100°C) [710], which is heated by passage of electrical current through the rod. Large electrical energy requirements are necessary because of the endothermic reaction, radiation heat losses, and incomplete conversion of the

TABLE 1 Estimation of Product Cost for Siemens Process

	Cost (1988 \$/kg Si)
Direct manufacturing cost	17.38
Raw materials	
Direct operating labor	
Utilities	
Supervision and clerical	
Maintenance and repairs	
Operating supplies	
Laboratory charge	
Indirect manufacturing cost	8.42
Depreciation	
Local taxes	
Insurance	
Plant overhead	1.90
General expenses	4.16
Administration	
Distribution and sales	
Research and development	

Product cost without profit	31.86
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TCS. Unreacted chlorosilanes, hydrogen chloride, and hydrogen are separated and recycled.

In the chemical engineering analysis of the process, a process design was performed for a plant to produce 1,000 t/year of polysilicon. The design included TCS production in a fluidized bed reactor; TCS purification by distillation; silicon production by chemical vapor deposition in a hot rod reactor; recycle of chlorosilanes, hydrogen chloride, and hydrogen; waste treatment provisions to meet environmental quality requirements and storage considerations for feed, in-process, and product materials. The process design provided detailed data for raw materials, utilities, major process equipment, and production labor requirements that are necessary for polysilicon production.

TABLE 2 Economic Summary: Cost Analysis for Siemens Process

1. Process	Siemens
2. Plant size	1000 MT/year
3. Plant product	Polysilicon
4. Plant investment	\$74.50 million
Fixed capital	\$64.80 million
Working capital	\$9.70 million
Total capital	\$74.50 million

5. Profitability analysis: return on original investment after taxes

(%ROI); discounted cash flow rate of return after taxes (%DCF)

Return (%ROI)	Sales Price (\$/kg Si)	Return (%DCF)	Sales Price (\$/kg Si)
0	31.86	0	31.86
10	45.66	10	41.19
20	59.46	20	52.08
30	73.26	30	64.07
40	87.06	40	76.78
50	100.86	50	89.92
60	114.66	60	103.32
70	128.46	70	116.88
80	142.26	80	130.53
90	156.06	90	144.24
100	169.86	100	157.98

Based on 10 year project life and 10 year straight line depreciation; tax rate (federal) of 46%

6. Sensitivity analysis

	Product Cost (\$/kg Si)					
	-50%	Base	+50%	+100%	Δ	
Raw materials	27.44	29.65	31.86	34.07	36.28	4.42
Labor	29.81	30.83	31.86	32.88	33.91	2.05
Utilities	23.51	27.68	31.86	36.03	40.21	8.35
Plant investment (fixed capital)	19.38	25.62	31.86	38.10	44.34	12.48

Note: 1988 dollars

Economics and Cost Analysis

The cost analysis results for producing polysilicon by the Siemens process are presented in Table 1, including costs for raw materials, labor, utilities, and other items comprising the product cost (total cost of producing product). The tabulation summarizes all these items to give a total product cost without profit of about 31.9\$/kg Si (1988 dollars). This product cost without profit includes direct manufacturing cost, indirect manufacturing cost, plant overhead, and general expenses.

The economic summary for the process is given in Table 2. The results for process, plant size, plant product, plant investment, profitability analysis and sensitivity analysis are displayed in the tabulation.

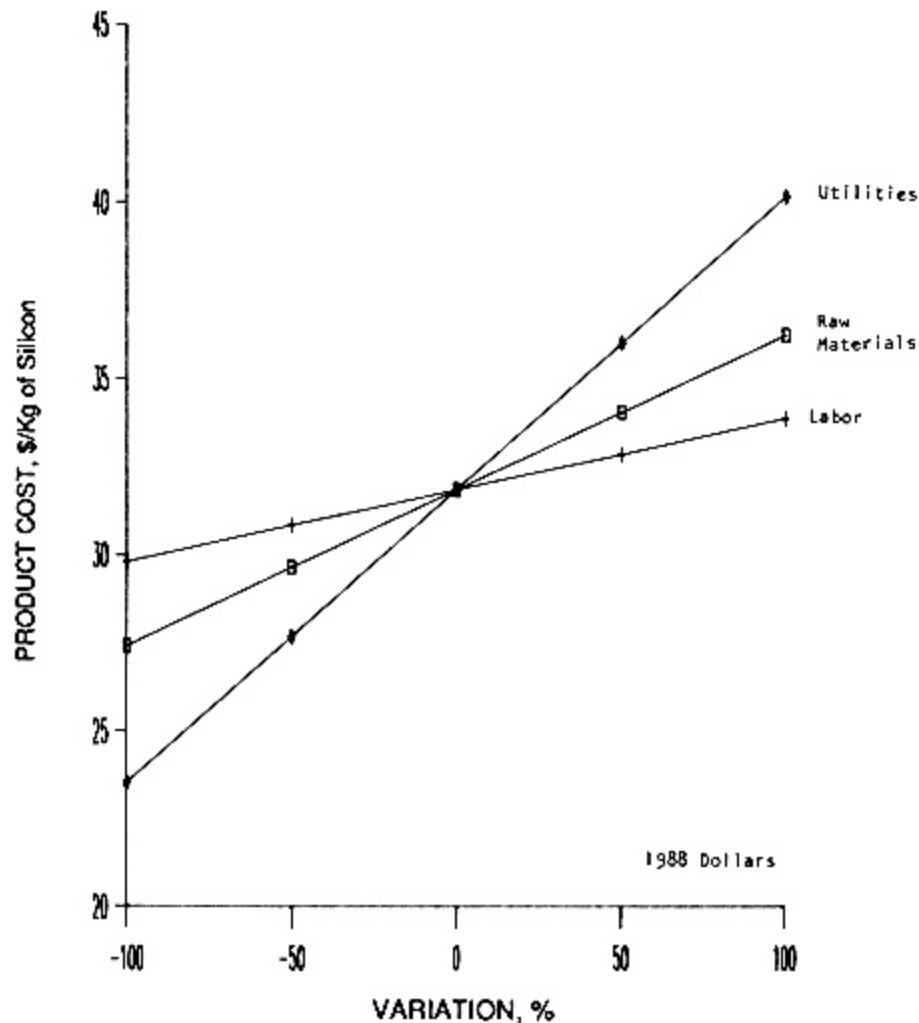


Fig. 4
Sensitivity plot for Siemens process.

A sensitivity analysis was performed to determine the influence of cost parameters on the economics of producing silicon by the process. The cost sensitivity results are given in Fig. 4, in which product cost (\$/kg Si) is plotted versus variation (-100 to 0 to 100%) of the primary cost parameters (raw materials, labor, and utilities). The 0% variation represents the base case. The -100% variation corresponds to the case of no costs for the parameter, and the +100% represents the case for a doubling of cost for each parameter.

The plot illustrates that product cost is influenced most by utilities and least by labor. Raw materials are intermediate in influence on the product cost. Electrical energy, which is used to achieve and maintain the hot rod surface temperature during long deposition runs, comprises the major portion of the utilities cost.

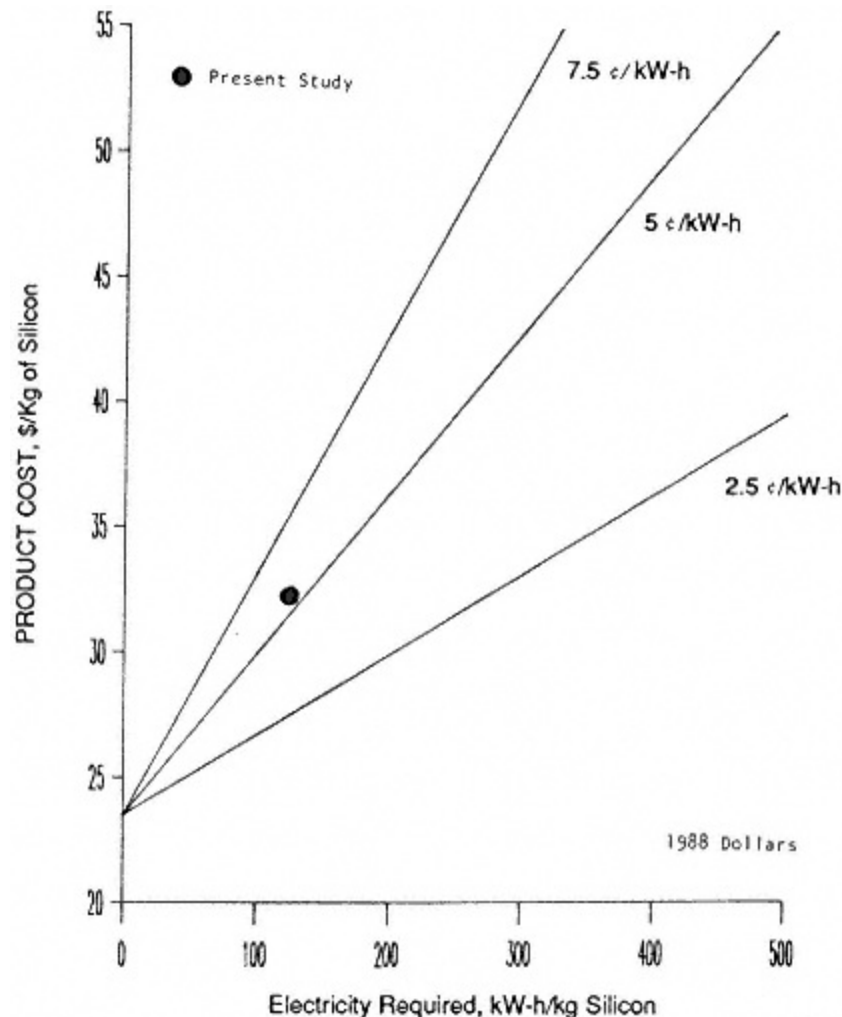


Fig. 5
Product cost versus electricity requirements for Siemens process.

The variation in product cost with electrical energy requirements (kW-h/kg Si) is shown in Fig. 5. The present study, which is based on electrical energy requirements of 120 kW-h/kg of Si and 5.4¢/kW-h of electricity, is shown as the darkened circle in the figure. If electrical energy requirements are increased from 120 to 240 kW-h, the product cost increases from \$31.9 to \$40.2 per kg Si. The increase is even more pronounced at 7.5¢/kW-h electricity.

Union Carbide Process

Process Description and Design

The flowsheet for the Union Carbide process is shown in Fig. 6. Hydrogen, silicon tetrachloride, and metallurgical-grade silicon are fed to the hydrogenation reactor (fluidized bed, 500°C, 515 psia, copper catalyst) to produce a mixture of chlorosilanes. The mixture of chlorosilanes from the hydrogenation reaction is condensed and subjected to several distillations to separate components and remove impurities.

Initially, the condensed liquid mixture is sent to D-01 stripper (90 psia) to remove inert gases and volatile impurities. The stripper bottoms go to D-02 distillation (55 psia), which separates TCS and TET. The TCS redis-

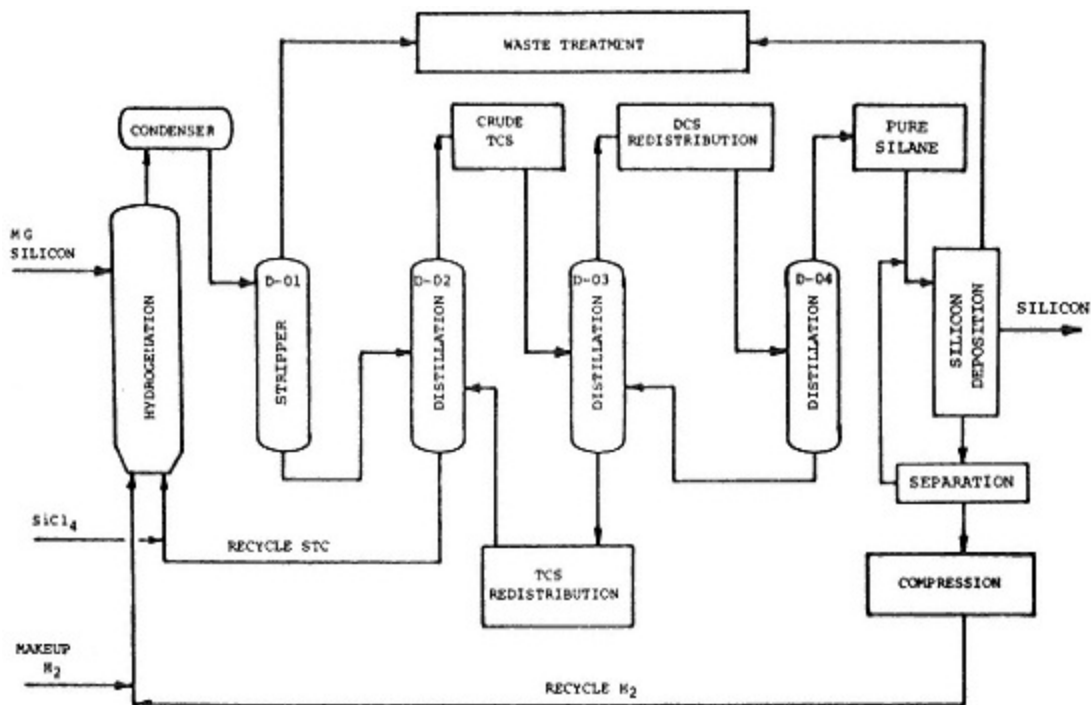


Fig. 6
Union Carbide process.

tribution reactor (liquid phase, 85 psia, 140°F, catalyst) is used to produce DCS (dichlorosilane). The separation of DCS and TCS is achieved in D-03 distillation (320 psia). The overhead goes to DCS redistribution reactor (liquid phase, 10 psia, 140°F, catalyst) to produce silane (SiH_4). The silane is purified by separation from trace impurities (such as B_2H_6) by D-04 distillation (355 psia).

The purity of the silane from the distillation is very high, with only parts per billion of electrically active impurities. Representative results for diborane impurity removal from silane are shown in Fig. 7.

The purified silane is mixed with hydrogen and then introduced into the chemical vapor deposition reactor (Komatsu license, Ref 1) to produce

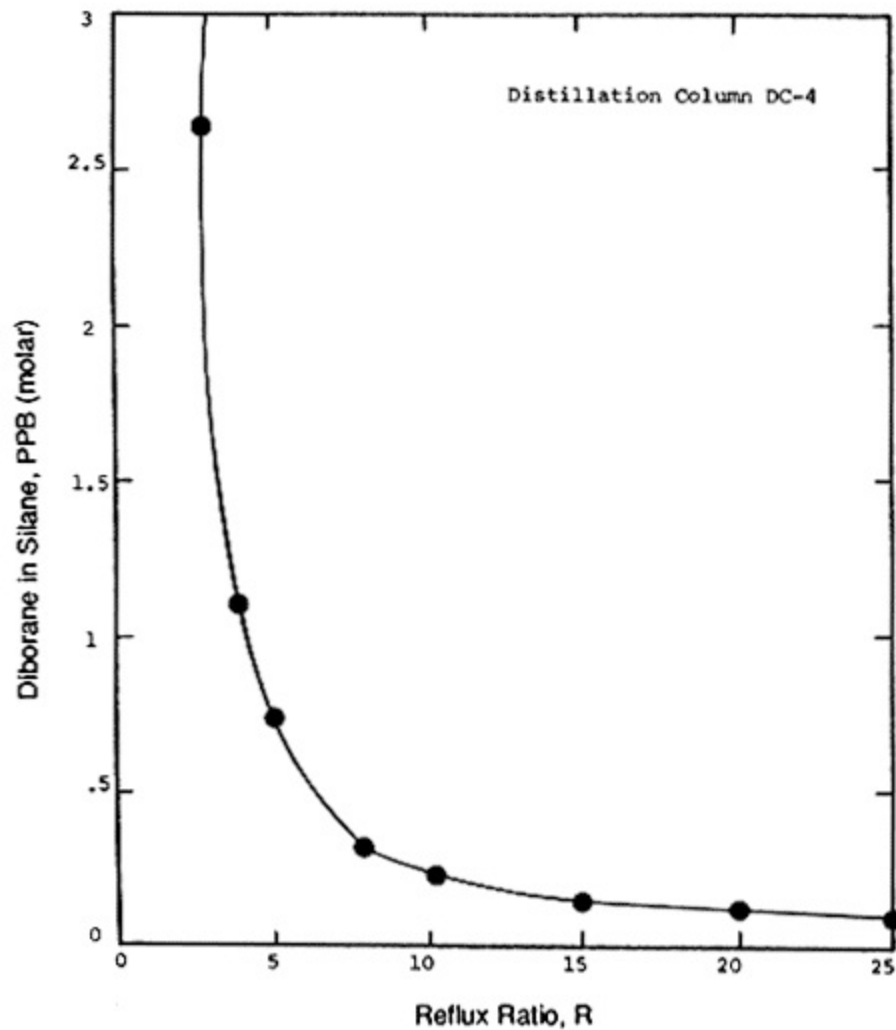


Fig. 7.
Representative results for diborane impurity removal.

silicon via the representative decomposition reaction



The reaction occurs in a deposition reactor heated by the passage of electrical current through the silicon rods to attain a temperature in the 800900°C range. Deposition rates of 48 μ/min of silicon on the rod surface are reported [2, 3].

For the deposition reactor, the homogeneous decomposition reaction resulting in silicon dust formation is not desirable. The heterogeneous decomposition reaction resulting in silicon deposition on the rod surface is desirable. The temperature dependence of critical silane concentration for homogeneous and heterogeneous decomposition regions has been studied [46]. At 800°C, the heterogeneous decomposition region appears to be in the 12% concentration range for silane in hydrogen.

In the chemical engineering analysis of the process, a process design was performed for a plant to produce 1,000 t/year of polysilicon. The design included TCS production in the hydrogenation unit; stripping to remove volatiles; redistribution reactors to produce silane; a distillation train to separate chlorosilanes; silane purification by distillation; silicon production by chemical vapor deposition of silane in a hot rod reactor; recycle of hydrogen; waste treatment provisions to meet environmental quality requirements; and storage considerations for feed, in-process, and product materials.

TABLE 3 Estimation of Product Cost for Union Carbide Process

	Cost (1988 \$/kg Si)
Direct manufacturing cost	12.09
Raw materials	
Direct operating labor	
Utilities	
Supervision and clerical	
Maintenance and repairs	
Operating supplies	
Laboratory charge	
Indirect manufacturing cost	9.13
Depreciation	
Local taxes	
Insurance	
Plant overhead	1.94
General expenses	3.47
Administration	
Distribution and sales	
Research and development	
Product cost without profit	26.63

Economics and Cost Analysis

Table 3 presents cost analysis results for producing polysilicon by the Union Carbide process. Table 3 indicates a total product cost without profit of about 26.6\$/kg Si (1988 dollars). This includes costs for raw materials, labor, utilities, and other items comprising the total cost of producing the product.

Table 4 summarizes the Union Carbide process. This includes the results for process, plant size, plant product, plant investment, profitability analysis, and sensitivity analysis.

The results for cost sensitivity are shown in Fig. 8 by plotting product cost as a function of the primary cost parameters (raw materials, labor, and utilities). The plot discloses that the product cost is influenced most by utilities. Raw materials are intermediate in effect on the product cost. Labor has the least effect.

TABLE 4 Economic Summary: Cost Analysis for Union Carbide Process

1. Process	Union Carbide
2. Plant size	1,000 MT/year
3. Plant product	Polysilicon
4. Plant investment	\$80.70 million
Fixed capital	\$70.20 million
Working capital	\$10.50 million
Total capital	\$80.70 million

5. Profitability analysis: return on original investment after taxes (%ROI):
discounted cash flow rate of return after taxes (%DCF)

Return (%ROI)	Sales Price (\$/kg Si)	Return (%DCF)	Sales Price (\$/kg Si)
0	26.63	0	26.63
10	41.58	10	36.74
20	56.53	20	48.54
30	71.48	30	61.53
40	86.43	40	75.29
50	101.38	50	89.53
60	116.33	60	104.05
70	131.28	70	118.74
80	146.23	80	133.52
90	161.18	90	148.37
100	176.13	100	163.26

Based on 10 year project life and 10 year straight line depreciation; tax
rate (federal) of 46%

6. Sensitivity analysis

	Product Cost (\$/kg Si)					
	-50%	Base	+50%	+100%	Δ	
Raw materials	23.49	25.06	26.63	28.20	29.77	3.14
Labor	24.58	25.61	26.63	27.66	28.68	2.05
Utilities	22.45	24.54	26.63	28.72	30.81	4.18
Plant investment (fixed capital)	13.11	19.87	26.63	33.39	40.15	13.52

Note: 1988 dollars

The major portion of utilities is comprised of electrical energy, which is required to heat and maintain the hot rod surface temperature during the long deposition runs. The variation in product cost with electrical energy requirements is given in Fig. 9. The present study is based on electrical energy requirements of 60 kW-h/kg Si and 5.4¢/kW-h of electricity. This is shown as the darkened circle in the figure. If electrical energy requirements are increased from 60 to 120 kW-h, the product cost increases from about \$26.6 to \$31.8 per kg Si. The increase in product cost is even more assertive at 7.5¢/kW-h of electricity.

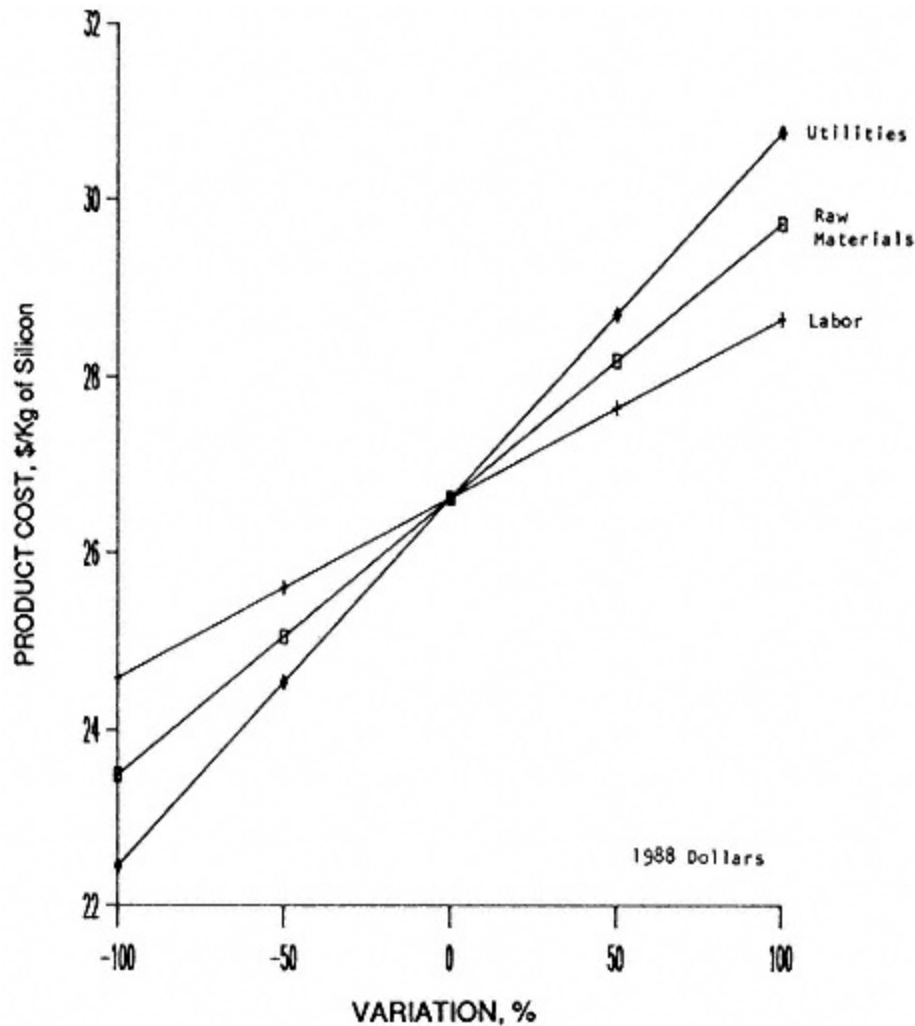


Fig. 8
Sensitivity plot for Union Carbide process.

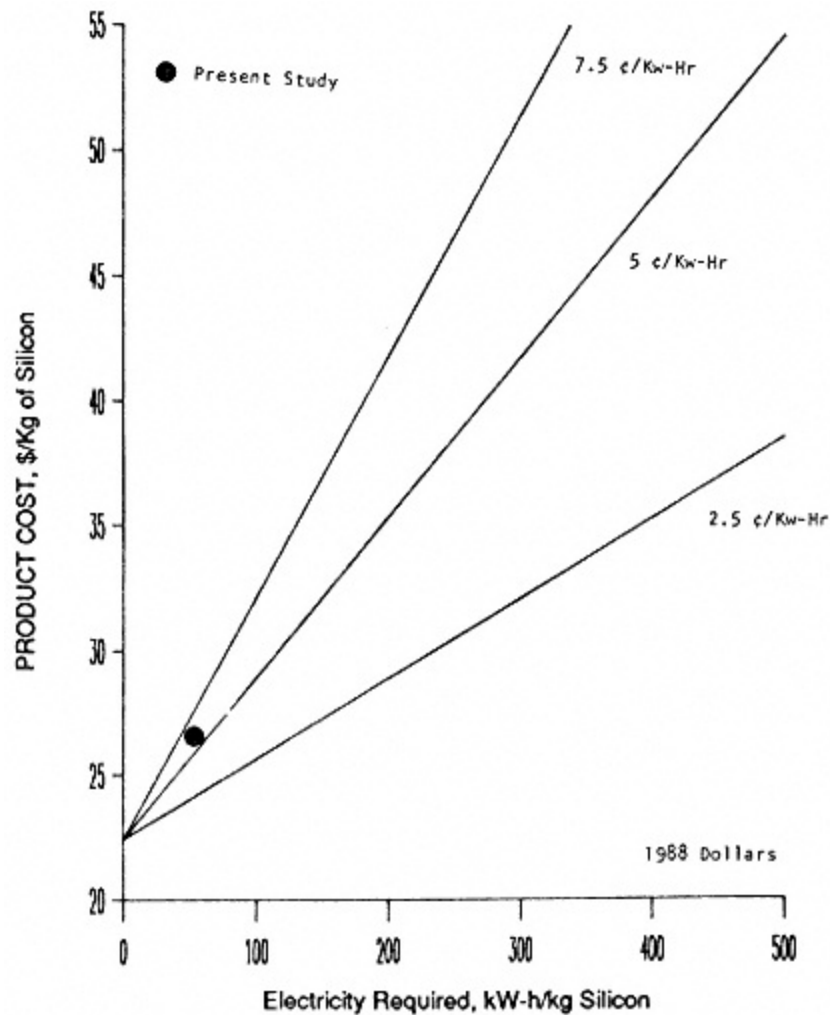


Fig. 9

Product cost versus electricity requirements for Union Carbide process.

Summary and Conclusions

The economics for producing polysilicon of semiconductor-grade purity in a 1,000 t/year plant are presented for the Siemens process (hydrogen reduction of trichlorosilane) and Union Carbide process (silane decomposition).

For the Siemens process using trichlorosilane, the product cost without profit is about 31.9\$/kg Si (1988 dollars). This product cost includes provisions for hydrogen chloride recycle and chlorosilane recycle: Without such raw material recycle, the product cost is higher. The product cost also in-

cludes low electrical usage (120 kW-H/kg Si). If higher electrical usage is required, the product cost is higher.

For the Union Carbide process using silane, the product cost without profit is about 26.6\$/kg Si (1988 dollars). This product cost assumes reasonable resolution of the homogeneous gas-phase decomposition reaction. Electrical usage is estimated at 60 kW-h/kg Si. If higher electrical usage is required, the product cost is higher. At electrical usage of 120 kW-h/kg Si, the product cost is about 31.8\$/kg Si.

The economics of producing polysilicon presented in this study are intended for use in initial project studies.

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