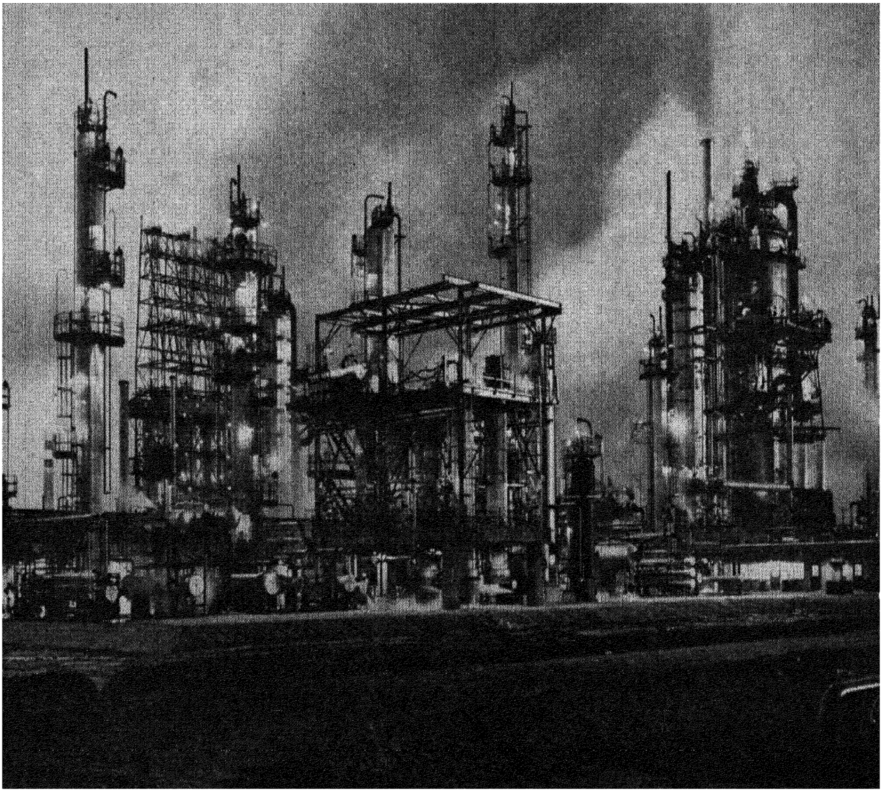
PETROLEUM PROCESSING

Principles
and
Applications



PETROLEUM PROCESSING

Principles and Applications

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Dedicated to
MY MOTHER

PREFACE

The origins of this book date back at least 15 years—to the first course in Applied Petroleum Processing offered to chemists and engineers at the Whiting Research Laboratory of the Standard Oil Co. (Indiana). Designed to acquaint the student with the practical aspects of refining procedures, the course proved very popular, and it has been repeated every two years. Four Standard Oil engineers have served successively as lecturers.

Because a text suitable for such a course has not been available, it has been taught from notes prepared by the lecturers. For each new class, the notes were reorganized and expanded to reflect the developing technology. Inasmuch as I have served as lecturer for the past three classes, this effort constitutes my fourth complete version.

The book is intended for people with a wide variety of backgrounds—for process-design engineers, mechanical-design engineers, operating men, technical-service engineers, research workers, patent lawyers—in fact, for anyone interested in the technology of petroleum refining. I have attempted to describe all major refining processes concisely, to point up their important aspects, to discuss each process in broad terms, and to provide references to sources of more detailed information. An expert on any process will probably find little new information on his specialty, but few people are experts in more than one or two fields.

In writing this book, I am indebted to the lecturers that preceded me—to Arthur L. Conn, James F. Vanecek, and James A. Bock. I am also indebted to the many experts at the Whiting Research Laboratory of the Standard Oil Co. (Indiana), who reviewed parts of the manuscript, and especially to William W. Sanders, who reviewed all of it.

R. J. Hengstebeck

CONTENTS

CHAPTER 1

PRODUCTS AND RAW MATERIALS

A petroleum refinery is a vast complex of towers, furnaces, reactors, pumps, compressors, heat exchangers, and tanks. What makes a refinery so complex? Probably the major factor is the multitude of products that are made—products ranging from liquefied gases for home cooking to asphalts for roofing and for road construction. Each of these products has its individual requirements, depending upon the uses to which it will be put. To understand petroleum refining, one must know what properties are desirable in each product, and what specifications must be met, for product specifications usually dictate refining operations. Some knowledge of the raw materials—crude oils—is also needed.

PRODUCTS

A complete discussion of all petroleum products would be very useful, but it would also be very lengthy. Here, only the principal products will be considered, and their uses and properties will be explored just sufficiently to provide the background needed for understanding refining operations. In order of decreasing volatility, the principal products are liquefied petroleum gases, gasolines, distillate and jet fuels, lubricating oils, waxes, greases, and asphalts and other residues.

Liquefied Petroleum Gases

The lightest materials produced in refining are gases at atmospheric pressure—hydrogen, methane, ethane and ethylene, propane and propene, and butanes and butenes. Except for butanes, a considerable portion of which is blended into gasoline, the bulk of these gases either is charged to further processing or is burned at the refinery as fuel. Some of the heavier gases are sold as liquefied petroleum gases, or LPG. From a processing standpoint, the production of LPG is a simple operation, consisting of separating the desired materials from the other gases, condensing them under pressure, and removing all sulfur-containing compounds. There are five recognized grades (Table 1-1). In 1950, LPG production totaled 100,000,000 bbl (20),* about 30 per cent of which came from refineries; the rest came from natural-gas operations. In 1957, production totaled 165,000,000 bbl (80).

Table 1-1

Grade	Maximum vapor pressure at 100°F, psi	Composition
A	80	Butanes
B	100	Butanes; some propane
C	125	Butanes; propane
D	175	Propane; some butanes
E	200	Propane

Uses. LPG has three principal uses—as a motor fuel, as a chemical raw material, and for home cooking and heating. LPG is a high-quality, low-cost motor fuel, but storage and transportation problems have limited its use to farm and fleet operations. About 20,000,000 bbl were so consumed in 1957 (11). Use of LPG as a raw material for the manufacture of chemicals is rapidly expanding; in 1957 it was 40,000,000 bbl (11,80). However, home cooking and heating account for the largest usage of LPG.

Motor Gasoline

Except for the earliest days of the petroleum industry, gasoline has been the principal product. Consequently, gasoline has received the greatest research attention, and manufacturing procedures have changed constantly as ways have been found to improve it. This situation will undoubtedly continue so long as gasoline engines are used to power automobiles. Gas turbines (30) and free-piston engines (5,97) are possible power plants of the future, but there is no agreement as to when, or even if, gasoline engines will be supplanted. How gasoline properties affect the operation of gasoline engines has been discussed in detail by Gruse and Stevens (42).

The production of motor gasolines in the United States in 1957 was almost 1,500,000,000 bbl (43).

Description. Motor gasolines are complex mixtures of liquid hydrocarbons, with boiling ranges of about 100 to 400°F† and with vapor pressures of about 10 psia. (The vapor pressure is somewhat higher in the winter; somewhat lower in the summer.) Most refiners market two grades—premium and regular—although a few market a single

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* Numbers in parentheses refer to the list of references at the end of each chapter.

† This is the ASTM boiling range (see Chap. 3). Gasolines usually contain appreciable amounts of materials whose true boiling points are outside this range. However, the true boiling points of most of the components are between 50 and 450°F.

intermediate grade, and a number sell a "superpremium." Gasolines are tailored for the engines that are to use them; thus specifications change as engines develop. As a general rule, premium gasolines are designed for late-model, high-performance engines.

Octane Number. Since about 1923, when tetraethyllead was introduced, the principal mark of gasoline quality has been resistance to knocking, which is expressed as "octane number."* Raising the octane number permits the engine designer to produce more powerful or more efficient engines by increasing compression ratios (67). Except during World War II, when high-octane components were diverted to aviation gasoline, octane numbers and compression ratios have been increasing steadily, as shown in Fig. 1-1. Octane and compression-ratio increases have been particularly striking since about 1950, and further increases are in prospect. As may be inferred from the figure, octane increments get "bigger," in terms of engine performance, as the octane level approaches 100 (77). Octane ratings above 100 are proportional to their performance potentials. There is some feeling that the practical octane ceiling is now being approached, but this remains to be demonstrated.

The octane quality of a gasoline may be rated differently by different engines. How production engines rate gasolines on the road is the important factor, of course, but such ratings are too time-consuming and too expensive to be used as specifications. Laboratory test procedures have therefore been adopted. Two are in use currently, the "research" and "motor" methods (4), which differ as to such details as engine speed and operating temperature. Depending upon the particular characteristics of production engines at a given time, one or the other method has approximated actual road ratings best. For some time, research ratings have been the principal standard, although road ratings with current engines usually fall between the research and motor numbers (24,32). Tetraethyllead is included in most gasolines to raise their

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* Octane number is an arbitrary scale based on the performances of mixtures of *i*-octane (2,2,4-trimethylpentane), which is resistant to knocking, and *n*-heptane, which is prone to knock. A 70-octane gasoline has the same knocking tendency as a mixture of 70 per cent *i*-octane and 30 per cent *n*-heptane *when tested under the same conditions.* Because the relative knocking characteristics of fuels change with test conditions (83), the testing method must be specified. Some commercial gasolines are more resistant to knocking than is *i*-octane; consequently, it has been necessary to extend the octane scale beyond the 100 level. The extension is based on performance number, which is directly proportional to the power that can be obtained from a gasoline when used in an engine designed for it. The formula for octanes above 100 is

$$\text{Octane number} = \frac{\text{performance number} - 100}{3} + 100$$

octane numbers (60). Other materials have been proposed for the same purpose (74), and compounds of manganese appear to have promise (16).

Octane ratings of pure compounds can be predicted from their structures (9). Aromatics and highly branched paraffinic hydrocarbons have the highest octane numbers, *n*-paraffins the lowest. Naphthenes, olefins, and lightly branched paraffins are intermediate (61). Increasing the chain length of a paraffinic hydrocarbon lowers its octane number; *i*-pentane, for example, has a lower rating than *i*-butane. The rating of an olefin depends considerably on the test engine and the test conditions. In modern American automobile engines, olefins have lower road ratings than indicated by their research and motor numbers (32). The effective octane rating of any component in a mixture depends to some extent upon the nature of the materials with which it is blended (9).

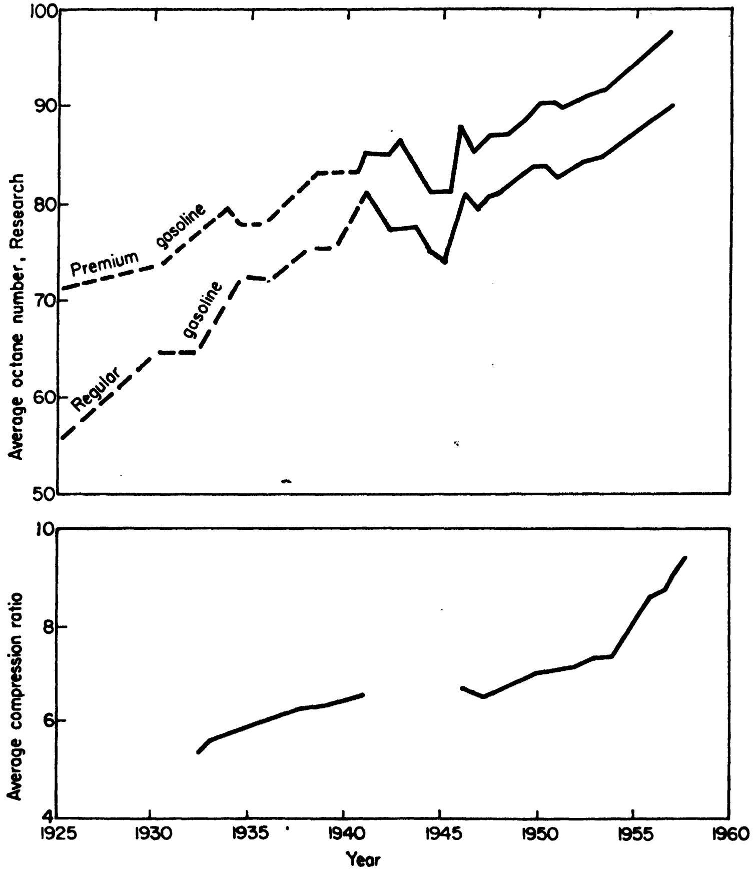

FIG. 1-1. Chronology of octane ratings and compression ratios.

Engine Deposits. Because combustion-chamber deposits increase the octane *requirement* of an engine, the deposit-forming tendencies of a gasoline are also important (98). Tetraethyllead is the principal contributor to the formation of deposits, but few gasolines are made without it; such gasolines are more costly to make and they command a premium price. There is some evidence that high-boiling components in gasoline increase deposits and octane requirements (36), but other evidence contradicts it (25). Any such effects of high-boiling components are minimized by the current multigraded lubricating oils. Deposit-modifying additives are added to some gasolines to make deposits less harmful (79).

Surface Ignition. The higher-compression engines made possible by higher octane gasolines have posed new problems—surface ignition (10) and spark-plug fouling. Raising the compression ratio increases engine temperatures. In modern engines, the temperatures are sometimes high enough to cause engine deposits to glow and to ignite the gasoline at the wrong time. A loss of power results, sometimes accompanied by erratic knocking or by a dull, thudding knock, and the fouling of spark plugs is accelerated. Phosphorus-containing additives are being used to suppress surface ignition and the fouling of spark plugs, but there is considerable controversy over their merits (19,35,51). They reduce the effectiveness of tetraethyllead (61), and some people think they do more harm than good (35).

Other Properties. Other motor-gasoline properties of importance are ease of starting, warm-up rate, tendency to vapor-lock, evaporation losses, and loss to the crankcase oil (3,54). All these properties are governed by the proportions of the various boiling-range materials included in the gasoline.

Ease of starting and warm-up rate* are improved by increasing the proportion of light ends, but more light ends also increase evaporation losses (83) and the tendency of the gasoline to vapor-lock. Careful balancing of these properties is necessary for the blending of satisfactory products (28). Because ease of starting, warm-up rate, evaporation losses, and tendency to vapor-lock all change with atmospheric temperature, the optimum amount of light ends varies with the seasons. If expressed as "the per cent boiling below 158°F," the optimum light-ends concentrations range from a minimum of about 20 per cent in the summer to a maximum of about 35 per cent in the winter. Gasoline vapor pressure and the 0 to 10 per cent slope of the distillation curve are also used as criteria for blending gasolines of satisfactory volatility (59).

Loss to the crankcase oil is important because it degrades the lubricating oil; the loss increases as the proportion of heavy ends increases. The

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* In 1957 cars the control point for warm-up performance shifted to the range of 50 to 70 per cent distilled (65).

National Bureau of Standards has set the maximum end point of gasoline at 437°F (3), but most gasolines have lower end points.

Properties of lesser importance are sulfur content and "gum" content. The importance of sulfur is debatable. Although experimental work (50) indicates that sulfur contributes to engine wear under stop-and-go driving conditions, gasolines with sulfur contents as high as 0.4 per cent have been marketed on the West Coast with no obvious disability, and most gasolines contain less than 0.1 per cent. Gasoline containing appreciable quantities in the form of mercaptans have an offensive odor and are called "sour"; however, a simple treatment renders them "sweet." Probably the most important effect of sulfur is its antagonistic effect on tetraethyllead (60,96).

"Gum" is formed by oxidation of certain components of gasoline. Although gum is soluble in gasoline, it deposits in the intake system of the engine when the gasoline evaporates. In most gasolines, the formation of gum is easily prevented by the addition of small amounts of chemical inhibitors (3,56). When inhibitors prove inadequate, processing is required to remove potential gum formers. Many gasolines include "metal deactivators" which counteract the oxidative catalytic effect of traces of metals dissolved in the gasolines.

Other additives are also blended into gasoline in small quantities to improve specific properties. Inhibitors are sometimes used to minimize corrosion, particularly of product pipe lines; these additives also reduce rusting of the customer's fuel system, although such rusting is seldom a problem without additives. Additives are also used in winter gasolines to prevent icing in carburetors and freezing in fuel lines. (Icing of carburetors results from expansion of the fuel-air mixture, which may lower temperatures to the point that atmospheric moisture freezes out (28). Freezing of fuel lines may result from traces of water in gasoline.) A small amount of a light lubricant is sometimes blended into gasoline to assist in the lubrication of valve stems and cylinders (56).

Aviation Gasolines

In comparison with motor gasolines, aviation gasolines have a narrower boiling range and a lower vapor pressure. Until about 1955, they were also of higher octane quality, but some motor gasolines are now in the aviation octane range. There are three principal grades of aviation gasolines, 91–98, 100–130, and 115–145. The first of each pair of numbers is a measure of lean mixture or cruising performance; the second is a measure of rich mixture or full-throttle performance. Principal components of high-octane aviation gasolines are aromatics and highly branched paraffins.

Because of the trend to jet engines in aircraft, little further development of aviation gasolines is anticipated. In 1950, American consumption was about 35,000,000 bbl (3).

Distillate Fuels and Jet Fuels

Distillate fuels are petroleum stocks that boil in the range of 350 to 700°F and have flash points* of 120°F or higher. They include kerosene, heating oils (No. 1 and No. 2 fuel oils†) and diesel fuels. In the early days of the industry, distillate fuels were the prime products. Now, and for some time past, they have ranked second to gasoline.

Jet fuels are similar to distillate fuels, except that the major production (for military uses) has been lower-boiling, with lower flash points. For commercial jet fuels, kerosenes are preferred because of their general availability; however, foreign kerosenes are lower-boiling than domestic stocks, and this difference constitutes a problem for intercontinental aircraft (43).

Burning Quality. Distillate fuels and jet fuels are similar in that performance depends on cleanliness of combustion. Cleanliness of combustion is measured by the "smoke point" of the fuel, which is the height of the highest flame that can be produced in a standard lamp without smoking (49,104).

Smoke points of hydrocarbons line up in the decreasing order: paraffins, naphthenes, olefins, simple aromatics, and condensed-ring aromatics. Consequently, virgin stocks,‡ which are made up of paraffins, naphthenes, and some simple aromatics, are superior to aromatic-rich cracked stocks§ for jet and distillate fuels. Kerosenes and No. 1 fuel oils are virgin products. Good kerosenes contain few aromatics (40,53), while No. 1 fuel oils contain up to 20 per cent; No. 2 fuel oils generally include substantial amounts of catalytically cracked stocks, which contain condensed-ring aromatics. Cracked stocks constitute at least 70 per cent of the No. 2 oil sold in the United States (45). Diesel fuels are usually similar to No. 1 and No. 2 fuel oils, although lower-grade stocks have also been produced for marine and stationary use and for railroads on an experimental basis (89). Engine development may facilitate the burning of lower-quality fuels (46).

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* The flash point is the temperature at which sufficient vapors evolve to form an explosive mixture with air. Normally, a liquid will not catch fire at its flash point; a temperature 40 to 50° higher is usually required (53).

† No. 1 fuel oil is "intended for vaporizing pot-type burners"; No. 2 fuel oil is "for general-purpose domestic heating," particularly for gun-type atomizing burners (45).

‡ Virgin stocks are materials separated from petroleum by physical methods, such as distillation.

§ Cracked stocks are produced by breaking larger molecules into smaller ones.

Distillate Fuels

Kerosenes are more volatile than heating oils, and No. 1 fuel oil is more volatile than No. 2. Premium diesel fuels correspond to No. 1 oil, regular diesel fuels correspond to No. 2 oil, and economy diesel fuels are higher boiling. Economy diesel fuels also contain more sulfur, which may contribute to engine wear (89). Typical inspections of distillate fuels are given in Table 1-2. Premium diesel fuels and No. 1 fuel oils are often sold interchangeably, as are regular diesel fuels and No. 2 fuel oils.

Table 1-2

Fuel	Smoke point[a]	Flash, °F	Boiling range, °F	°API	Per cent sulfur	Diesel index[b]	Cetane No.[c]
Kerosene	28	120	340–510	43	0.04	65+	
No. 1 fuel oil	26	135	360–570	41	0.2	60	55
No. 2 fuel oil	20	140	380–650	36	0.3	50	50
Economy diesel fuel	. .	170	430–700	27	1.0	30	40

[a] British Institute of Petroleum, 57/48.

[b] Diesel index = (°API) × (aniline point, °F) ÷ 100.

[c] Cetane number (52) indicates the cetane-alpha methylnaphthalene mixture (per cent cetane) that gives the same performance in a diesel engine as does the test fuel (53). A fuel with a high cetane number has a low octane number, and vice versa. The cetane number of a fuel can be improved by the addition of an "ignition improver," e.g., amyl nitrate (56).

Stability. Stability is a problem in the blending of No. 2 fuel oils and regular diesel fuels. Both are usually blended from catalytic cycle stocks and virgin stocks, which are often incompatible to some degree. Dispersant-type additives are added to about 75 per cent of the current No. 2 oil production to prevent the sludging that could result from incompatibility (12). The additives often supply additional protection—for example, against the formation of gummy materials or against corrosion.

Other Properties. Other qualities of some importance are low freezing points, to permit flow in cold weather, and low sulfur contents, to minimize corrosion and odor problems (53,88) and wear in diesel engines (31). The No. 1 fuel must contain sufficient light ends to ensure quick starting in vaporizing burners (45). When it is sold for use in pipeless space heaters, No. 1 fuel must also be free from objectionable odors, both in the fuel and in its combustion products (17,45).

Production. In 1957, the United States production of distillate fuels was almost 800,000,000 bbl, or about 27 per cent of the crude run (43).

Jet Fuels

Jet fuels must be clean burning. For commercial fuels, proposed specifications are given in Table 1-3 (44). Freezing point is specified because of the low temperatures encountered at high altitudes. For the same reason, additives such as isopropyl alcohol may be added to avoid the freezing of traces of water. Jet fuels for high-performance military engines usually have a lower freezing-point specification (−76°F maximum).

Table 1-3

Property	*Proposed specifications*
ASTM 10 per cent point, °F	392, maximum
ASTM 50 per cent point, °F	440, maximum
ASTM 90 per cent point, °F	500, maximum
ASTM end point, °F	572, maximum
Gravity, °API	40–48, possibly 38–50
Freezing point, °F	−40 to −58, maximum
Sulfur content, per cent	0.2 to 0.4, maximum
Aromatics content, per cent	20, maximum

In aircraft designed for supersonic speeds, the fuel itself is the only practical coolant for the engine. Air-coolant systems would have severe drag penalties, and surface air is heated to over 200°F by friction (12). When used as a coolant, the fuel is subjected to high temperatures; nevertheless, it must not deposit "lacquers" on the heat-exchange surfaces or form even small amounts of gummy materials which could plug the filters and orifices through which the heated fuel is pumped. Dispersant-type additives are sometimes used to alleviate these problems (12).

Military fuels have been wider-boiling than commercial jet fuels, probably to ensure that an adequate supply would be available in the event of war. Several military grades have been established, but "JP-4" has accounted for the largest consumption. Table 1-4 gives typical inspections of JP-4 fuels (37). Even in peacetime, the demand for military jet fuels has been substantial. In 1955 military uses accounted for about 2 per cent of the crude run (62).

Table 1-4

Property	*Range*
Gravity, °API	45–55
ASTM 10 per cent point, °F	190–245
ASTM 90 per cent point, °F	400–460
Reid vapor pressure, lb	2.2–3.0
Freezing point, °F	−76
Smoke point, mm	23–29

Lubricating Oils

Originally lubricating oils were high-boiling, high-viscosity oil fractions from which undesirable components had been removed. As technology developed and as service requirements became more severe, additives were incorporated to improve performance. This trend has been particularly marked in recent years; additives now constitute a large part—perhaps the major part—of lubricating-oil technology (13,66,81).

Aircraft developments have created lubricating-oil demands that cannot be met by normal petroleum stocks. To meet these demands, "synthetic" lubricants are being produced (38). Although synthetic materials are superior lubricants for many purposes, their high costs will probably restrict their use to special services.

Because lubricating oils are made for a wide variety of applications, it is not possible to make a universal product to meet all requirements. Consequently, lubricating oils are formulated for particular applications, and a large variety is required. Because a desirable property cannot usually be maximized without adversely affecting other properties, lubricating oils represent compromises aimed at obtaining the best combinations of properties for given applications. Lubricating oils may be divided into three classifications: motor oils, industrial oils, and metalworking oils.

Motor Oils. Motor oils are used under very severe conditions, especially in diesel or in aircraft engines (55,81). In all internal-combustion engines, motor oils are exposed to hot surfaces near the combustion chambers. Oil is thrown off the surfaces in thin sheets that provide large areas for oxidation. Partially burned products of combustion enter the crankcase and react to form lacquer, sludge, and varnish, and abrasive dust finds its way into the crankcase. Inhibitors and detergents are included in motor oils to keep engines clean and thereby improve bearing, piston ring, and valve life. Nevertheless, accumulation of sludge and dust in the oil necessitates periodic oil changes, which are recommended every 1,000 to 3,000 miles, or after about 30 to 100 hr of operation.

Viscosity index is an important property of motor oils. It is an index of the resistance of an oil to "thinning out" as the temperature is raised (55). High viscosity index is desirable to permit ease of starting at low temperatures while minimizing leakage at operating temperatures. This property is particularly important for winter driving in northern climates. Lubricating oils must be fluid, of course, at the lowest temperatures at which they are used.

Motor oils are classified according to their viscosities and their detergencies. The viscosity classifications are as shown in Table 1-5. Recently, multigraded classifications have been introduced, for example, 10W-30. A 10W-30 oil has the low-temperature viscosity of a 10W oil, and the high-temperature viscosity of a 30 oil. A 10W-30 oil may be produced by adding a "viscosity-index improver," such as polybutene, to a 5W oil. Multigraded oils are advertised as all-weather oils. They minimize combustion-chamber deposits (and thus permit the use of lower-octane gasolines), reduce wear, and give increased gasoline mileage (85).

Table 1-5

SAE Number	Viscosity, Saybolt Universal (seconds) at			
	0°F		210°F	
	Min	Max	Min	Max
5W	......	4,000		
10W	6,000	12,000		
20W	12,000	48,000		
20	......	......	45	58
30	......	......	58	70
40	......	......	70	85
50	......	......	85	110

Detergency classifications of motor oils are, in the order of increasing detergency:

ML—for light service in gasoline engines
MM—for medium service in gasoline engines
MS—for severe service in gasoline engines
DG—for general service in diesel engines
DM—for severe service in diesel engines (high-sulfur fuel)
DS—for service in supercharged diesel engines

Lubricating oils affect combustion-chamber deposits and thus the octane requirements of the engines in which they are used. Octane requirements are lower when heavy components are eliminated from the oil (63,103).

Industrial Oils. Industrial oils (55) may be classified as to severity of service—light duty, moderate duty, and severe duty.

Light-duty services are typified by the lubrication of bearings in machine tools, stamping presses, and electric motors; straight mineral oils are used, with or without the addition of antioxidants and rust inhibitors (81).

Moderate-duty services are exemplified by steam turbines, which operate at higher loads and higher rubbing speeds, and with closer clearances (81). Because of the more severe requirements, such oils are circulated through coolers, and leakage often results in contamination with water. To minimize the adverse effects of water, good demulsibility (water-separation characteristics) is required. The major problem, however, is oxidation, and inhibitors are usually incorporated in the oils to make their useful lives as long as fifteen years.

Severe services are typified by the lubrication of steel-mill roll-stand bearings, and of gears, both of which operate at high loads (81). At moderately high loads, adequate lubrication can usually be obtained with high-viscosity oils. At higher loads, extreme-pressure agents* are required to prevent metal-to-metal contact and the wear that results from it. Antioxidants, antifoam agents, and antirust agents are often added to the oils.

Hydraulic and transmission oils have requirements similar to those for light-duty oils, except that they must operate over a wider temperature range; consequently, wax-free oils with high viscosity indexes are required. Antifoam agents are frequently employed in hydraulic and transmission oils.

Metalworking Oils. The largest classes of products used in metalworking operations are soluble oils and cutting oils (22). Strictly speaking, these are not lubricants. Their primary functions are to cool the tool and the part being machined, and to avoid the welding, galling, or seizure that results from metal-to-metal contact (81).

Although water is an excellent coolant for machining operations, it tends to rust metal surfaces. Soluble oils (more correctly, emulsifiable oils), when dispersed in water, provide rust protection and some lubricity without impairing the coolant properties of water. They are made by adding emulsifiers to a petroleum oil. Heavy-duty soluble oils also contain extreme-pressure agents to prevent metal-to-metal contact. Because extreme-pressure agents tend to stain nonferrous materials, they are used primarily in oils made for machining ferrous metals. A wide variety of soluble oils are required because their various applications differ widely. In use, soluble oils may be diluted to as low as 2 per cent concentration; a 10 per cent concentration is typical.

Cutting oils are petroleum oils containing extreme-pressure agents. They perform the same functions as do soluble oils, but they are not emulsified in water. Cutting oils operate at temperatures as high as 1000°F and at pressures as high as 200,000 psi (96).

Petroleum Waxes

Petroleum waxes fall into two categories: paraffin and microcrystalline (48,99). Paraffin waxes are white, relatively hard, translucent solids,

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* Extreme-pressure agents are materials that react with metal surfaces to form protective films. They usually contain chlorine, sulfur, and/or phosphorus compounds.

with melting points between 105°F and 180°F, usually between 120°F and 140°F. They contain large amounts of *n*-paraffins with 23 to 29 carbon atoms, and they are typified by the wax used in candles. Microcrystalline waxes are tough, flexible solids ranging in color from white to brown, with melting points in the range of 145 to 190°F (27). They consist of hydrocarbons with 34 to 70 carbon atoms "predominantly of the naphthene-containing paraffin structure" (48). Mixtures of microcrystalline wax with viscous hydrocarbon liquids are called petrolatums. In 1951, 1,120,000,000 lb of paraffin wax and 225,000,000 lb of microcrystalline wax were produced in the United States (99).

Eighty per cent of the paraffin wax produced in the United States is used to make waxed papers and cartons (27). Important properties in this use are sealing qualities, tensile strength, flexibility, moisture proofing, blocking characteristics (tendency of waxed papers to stick together (94)), and gloss of the finished product. Waxes with melting points of about 130°F are usually employed for waxed paper and cartons. Other consumers of paraffin waxes include candles, matches, rust preventives, fruit and vegetable coatings, electrical and communication equipment, and dental wax.

Warth lists 64 applications of microcrystalline wax, ranging from yarn lubrication to electrical insulation (99).

Petroleum Greases

Petroleum greases are semisolids formed by dispersion of 3 to 30 per cent of solid thickeners in petroleum oils. They are used where lubrication is required, but where a sealed system cannot be provided.

Physically, a grease may be visualized as a mesh made up of particles of thickener, the mesh absorbing oil as a sponge does water (18). To make the comparison exact, the sponge would have to be an "irreversible" one that held water tenaciously. A grease may also be regarded either as a gel-like system with weak intraparticle forces or as a sol-like system with weak interparticle attractions (58).

The properties of petroleum greases vary over a wide range—from very soft greases to hard bricklike greases, with melting points ranging from about 160°F to about 350°F,* and with varying resistances to water. Grease properties are determined by the viscosity of the oil and by the kind and amount of thickener used.

Grease production in the United States was 940,000,000 lb in 1955 (84).

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* For higher-temperature applications, synthetic oils are used in formulating greases. Certain greases, formulated with silicone oils, may be used at temperatures to 600°F. Silicones make versatile greases because their properties change slowly with temperature. Some silicone greases function satisfactorily from −65 to 450°F.

Types of Petroleum Greases. Petroleum greases may be differentiated according to the kind of thickener employed. There are four general classes of thickeners: metallic soaps, organic materials, special clays, and modified silicas. Metallic soaps are the oldest type, and they account for the largest volume.

Originally calcium soaps and sodium soaps were the preferred thickeners (81). Conventional calcium-soap greases are not susceptible to water, but their service temperatures are limited to about 180°F.* Sodium-soap greases may be used at temperatures as high as 300°F, but they are susceptible to water. Lithium-soap greases, which were first made about 1950, combine the best features of both of the earlier types. Since 1950, multipurpose greases, formulated with lithium, have taken the major share of the market, even though they cost more than calcium- and sodium-based products. Aluminum- and barium-soap greases are also made in small volumes for specialized applications.

Petroleum greases made with organic thickeners (34,86,92), special clays (33), or modified silicas (64) may be used at temperatures up to 350°F; service temperatures are limited by the properties of petroleum oils. These greases, which have also been developed since 1950, may displace soap-based greases for most applications.

Specialty greases are also made in relatively small volumes. An interesting example is "rheopectic" greases (68). Rheopectic greases are oils until "worked"—by passage through a small tube, for example. They are used in automatic self-lubricators, in which they "set up" when forced through the dispensing tubes.

Classifications. Greases are classified according to hardness, or consistency. Consistency is measured by the depth of penetration of a standard cone under prescribed conditions.

Asphalts

Asphalts are the least understood of the major petroleum products, probably because they are complex materials of relatively low value. They are generally considered to be colloids of "asphaltenes" and "resins" in oils (8,48). Asphaltenes are brownish-black solids soluble in benzene, but not in light paraffinic solvents; they swell on heating and then decompose into cokelike substances. Chemically, asphaltenes are made up principally of carbon and hydrogen, with appreciable concentrations of sulfur, oxygen, and nitrogen. Resins are highly adhesive, brown, semisolid materials. A typical paving asphalt may contain 28 per cent asphaltenes and 40 per cent resins (8).

Asphalts are produced from the heaviest portions of certain crudes

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* Modified calcium-soap greases can be used at higher temperatures.

(8), the yield depending upon the crude. Yields as high as 65 per cent have been obtained from heavy crudes (1). The most important physical property is consistency, which is measured empirically by the depth of penetration of a weighted needle in a standard test. Other important properties are softening point, resiliency, ductility, and tensile strength. Properties of asphalts from aromatic crudes are affected most by temperature, properties of asphalts from paraffinic crudes are affected least, and asphalts from naphthenic crudes are intermediate. A high wax content is objectionable in asphalts because it reduces adhesiveness and low-temperature flexibility.

Asphalts are found in large deposits, and such "natural asphalts" were used for paving as early as 1852. Asphalt was first produced from petroleum on a commercial scale in 1894. Use of the petroleum product has grown continuously since then, and in 1911 it passed natural asphalt. In 1949, the consumption of petroleum asphalt was more than 9,000,000 tons, about 3 per cent of the national crude run and eight times the consumption of the natural product (48). Approximately 64 per cent was used for paving, 26 per cent for roofing and the remaining 10 per cent for miscellaneous uses, including road oils. About 40 per cent of the paving asphalt was marketed as cutback asphalts, i.e., mixtures of asphalts in lower-boiling materials that evaporate after application. In 1957, asphalt production in the United States was about 93,000,000 bbl (43), or about 16 million tons.

Asphalt pavements are intimate mixtures of "aggregate"—sand and gravel—and asphalt. In view of the generally satisfactory performance of asphalt roads, surprisingly little is known about their engineering properties, and specifications are empirical (14). Considerable work is now being done to obtain a more basic understanding of how asphalts perform (7,39,48,57,93).

Poor adhesion of asphalts to wet aggregate has long been a problem—often resulting either in expensive delays in construction or in inferior roads. Additives are now used to improve the bonding of wet aggregates and asphalts (26).

Residues

Residues from petroleum operations consist of heavy liquid fuels (resids) and solids (coke). Heavy liquid fuels are used in large stationary engines and in marine engines, and mixtures of distillate and residual fuels have been used experimentally in railroad diesels (23). Viscosity is the most important property of residual oils because of difficulties in handling and atomizing highly viscous oils. Ash and sulfur contents are also of some importance (23). Petroleum ash, particularly vanadium and sodium, attacks furnace refractories and turbine blades. Sulfur accentuates the ash problem, it may cause low-temperature corrosion in air heaters and economizers, and it contributes to air pollution.

Petroleum coke is used as a refinery and commercial fuel, in the manufacture of electrodes, abrasives, artificial graphite, and calcium carbide, and as a metallurgical fuel (95). Low sulfurcontent is required if petroleum coke is to be used in the manufacture of electrodes or as a metallurgical fuel. Electrode coke must be calcined to reduce its volatiles content (21).

Other Products

Other products include solvents, white oils, tractor and power fuels, and chemicals of various kinds.

Petroleum solvents are used in many industrial operations; a wide variety is produced to meet the requirements of each particular industry. In most cases, solvents boil within the gasoline range, but some extend into the kerosene range (53,71). There are two major classifications: low-solvency naphthas,* which are low in aromatics, and high-solvency naphthas, which are rich in aromatics. The cheaper low-solvency naphthas are used in paints, in dry cleaning, in the compounding of rubber, and in many other ways. The more expensive high-solvency naphthas are used in the manufacture of synthetic-resin finishes, lacquers, and other products for which a high dissolving power is required. In general, solvent naphthas must be resistant to oxidation, colorless, and have little odor.

White oils are oils in the lubricating oil range that have been drastically refined, usually with fuming sulfuric acid. There are two grades—technical and pharmaceutical. Technical white oils are used for cosmetics, textile lubrication, varnish compounding, and insecticide purposes. Pharmaceutical oils are employed as laxatives and for lubrication of food-handling machinery.

Tractor and power fuels are fuels in the gasoline-kerosene boiling range, but cheaper than either. In general, they are lighter than 36°API, and have octane numbers above 30.

CRUDE OILS

Petroleum oils, or crude oils, are brownish-green to black liquids composed chiefly of carbon and hydrogen. Very complex mixtures, they contain many thousands of individual compounds, ranging from light gases, such as methane, to heavy asphaltic materials that are solids when separated from the oil. The mixtures are very complex and analyses are very difficult. Despite the expenditure of much effort,

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* A naphtha is a volatile petroleum fraction, usually boiling in the gasoline range.

relatively few compounds—perhaps 150—have been isolated (87). Proportions of the various materials vary widely. Light crudes contain up to 75 per cent gasoline; the heaviest contain none. Lighter crudes are very fluid; some of the heavier crudes are so viscous they must be warmed for pumping.

Crude oil was first produced commercially in 1857, and production has increased continuously since then. In 1957, almost 3,000,000,000 bbl were consumed in the United States (43).

Origin of Petroleum

Although the origin of petroleum (41*a*) has occasioned much speculation, it remains one of the big mysteries of science. The most popular theory is based on organic source materials. It is postulated that animal or vegetable matter accumulated in favorable locations millions of years ago, for example, in swamps, in deltas, or in shallow seas. There the organic matter was partially decomposed by bacterial action, carbohydrates and proteins being broken down into gases or into water-soluble components that were dissolved in ground water and carried away. The remaining fats and fat-soluble materials were converted very slowly to petroleum through reactions that produced lower-boiling materials. The liquid petroleum that resulted could then migrate into natural sand or limestone reservoirs. At a temperature of 200°F, which is believed to be reasonable, catalysts would have been necessary for the presumed reactions to have occurred at the estimated ages of petroleum-bearing formations—generally less than 300 million years.* Natural catalysts are present in the earth. Radioactive materials are also present, and they may have accelerated the reaction.

This mechanism suggests that older crude oils should have reacted more completely, and, therefore, should contain more of the lighter products such as gasoline and kerosene. Qualitatively, this seems to be so; oil from deeper formations tends to be lighter.

Compositions of Petroleum Oils

The principal compounds in petroleum are aromatics, naphthenes, paraffins, and asphaltic materials. In the higher-boiling fractions, distinctions are somewhat arbitrary because individual molecules may contain large paraffinic groups attached to one or more naphthenic or aromatic rings. All compounds containing ring structures are classified as naphthenes or aromatics, even though they may contain more carbon atoms as chains than as rings. Consequently, except for a few crudes

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* Contrary to previous beliefs, a study made in 1957 suggests that petroleum may form in as little as 5,000 years (76).

in which asphaltic materials predominate, the ring compounds make up the bulk of each crude, generally constituting 60 to 90 per cent. Paraffins concentrate in the lower-boiling cuts, and asphaltic materials are found only in the high-boiling fractions. How the compositions of typical crudes change with boiling range is illustrated in Fig. 1-2.

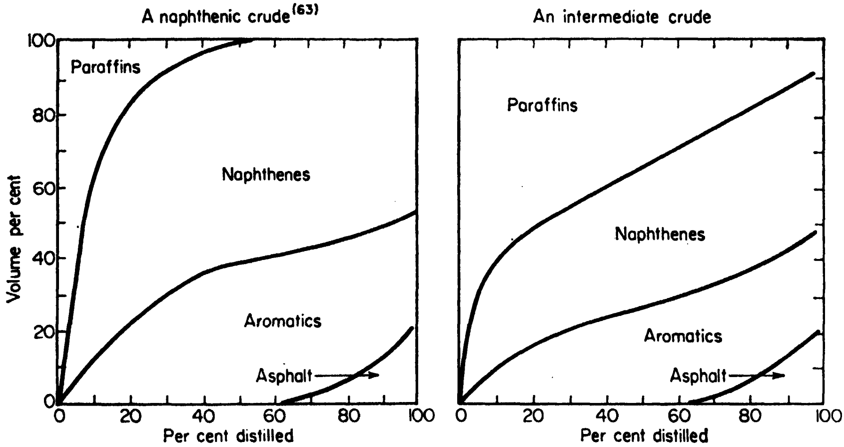

FIG. 1-2. Compositions of typical crude oils.

Despite wide variations in the chemical compositions and physical properties of crudes, their elemental compositions generally fall within the following narrow ranges:

Composition	*Per cent*
Carbon	84–87
Hydrogen	11–14
Sulfur	0–3
Nitrogen	0–1
Oxygen	0–2

This constancy occurs because a crude oil is composed of a few homologous series of hydrocarbons, each series having a fairly constant elemental composition. Incomplete decomposition of proteins could explain the sulfur and nitrogen contents; oxygen may come from the original source materials, or it may result from oxidation of intermediate products.

In a given crude, the concentrations of sulfur, nitrogen, and oxygen increase as boiling points increase. Sulfur is largely in the form of mercaptans and sulfides, although hydrogen sulfide and some free sulfur are sometimes present also (87). About half of the nitrogen compounds are basic; the other half includes pyrroles and, possibly, amides. Oxygen in the lower-boiling fractions is present as phenols and carboxylic acids. Higher-boiling oxygen compounds are principally asphalts.

In the compositions of virgin gasolines, the following generalizations have been noted (87):

1. The concentrations of four *n*-paraffins, hexane through nonane, are approximately equal.
2. Dimethylbutanes and methylpentanes are present in the approximate ratio 14:86.
3. Alkylcyclopentanes with five, six, and seven carbon atoms occur in the proportion 4:35:61.
4. Cyclohexane and methylcyclohexane occur in the ratio of 28:72.
5. Benzene, toluene, and C_8 alkylbenzenes are present in the proportion 7:31:62.

Evaluation of Petroleum Oils

The value of a petroleum oil depends primarily on its gasoline, distillate-fuels, and lubricating-oil contents. Both the qualities and the volumes of these materials are important. Because each of these quality and quantity properties is independent of the others, the evaluation of crudes is difficult, and no simple criterion is possible. The exact value of a given crude can be ascertained only by extensive tests to determine the yields and qualities of the several products, as well as the processing required to make them (2). The value of a crude also depends on where it is processed, because the relative proportions desired for the products vary from refinery to refinery and because the available processing equipment also varies. Inasmuch as refining techniques change constantly, the relative values of crude oils also change.

Yields and product qualities are usually estimated from empirical correlations of the physical properties of the several fractions of the crude oil.

Classifications

The quality of each of the principal fractions of a crude is determined by its composition. A rough indication of composition is provided by the Bureau of Mines "correlation index" (90), which is determined from specific gravity and boiling-point measurements (91). Other methods of classifying crudes have been discussed at length by Nelson (72). Properties of crude oils from various fields have been described in the literature (15,41,47,75,82,101).

Important Properties

Inspections of a crude oil do not define its quality because yields of products and their properties are not defined by inspections. General characteristics of a crude can usually be estimated from geographical location, although this criterion is sometimes misleading. If the general characteristics are known, inspections give some indication of quality. Among the more important properties are the following:

Gravity. The lighter the crude (the higher the °API), the larger is the content of the more valuable lighter constituents such as gasoline and kerosene. The normal range is 12 to 43°API.

Sulfur Content. The lower the sulfur content, the better the crude. High sulfur contents require more extensive refining procedures for the production of satisfactory products (70,102). They also promote the corrosion of refinery equipment. High-sulfur stocks are called "sour," particularly if the sulfur is corrosive, and low-sulfur stocks are called "sweet." There is no particular sulfur level which is recognized as a dividing line. The average sulfur content of American crudes is in the neighborhood of 0.6 per cent. About 40 per cent contain less than 0.25 per cent, and 7 per cent contain more than 2 per cent (87).

Nitrogen Content. A high nitrogen content is undesirable because nitrogen interferes with catalytic conversions and may cause product-stability problems. The average for American crude oils is 0.15 per cent; above 0.25 per cent is considered high. Most high-nitrogen crudes are found in California, although some Wyoming and Oklahoma crudes are moderately high (7).

Carbon Residue. Crudes with lower carbon residues are generally more valuable because they constitute better charge stocks for the manufacture of lubricating oils. The intermediate boiling-range materials are also better charge stocks for cracking. Carbon residue is determined by distillation to a coke residue in the absence of air. The usual range is 0.1 to 5 per cent, although carbon residue may be as high as 15 per cent.

Salt Content. Crude oils may contain up to 0.6 lb of salt per barrel of crude. Salt deposits in furnaces and heat exchangers and reduces their capacities, and chlorides may liberate hydrochloric acid and thereby promote corrosion. High salt contents require desalting before processing (78,100).

Viscosity. The usual range of viscosity is 40 to 60 SSU at 100°F, but it may range as high as 6,000 SSU at 100°F.

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CHAPTER 2

GENERAL OPERATIONS

Because the properties of crude oils are so varied and the possible products so numerous, the term "petroleum refinery" gives little indication of what operations are carried out at any given location, or what equipment is used. The one operation common to all refineries is distillation, which separates petroleum into fractions by boiling range. Other operations may be few or many, simple or complex, depending upon what products are made.

TYPES OF REFINERIES

The simplest refinery is one that processes a heavy crude oil to make asphalt as a primary product. In addition to the primary distillation unit, such a refinery may include facilities for converting into salable products the gasoline and distillate-fuels boiling-range materials distilled from the crude oil. Alternatively, these materials may be sold to another refiner. In either case, the distillate which is higher boiling than distillate fuels is usually sold for further processing.

Next in complexity is the refinery that produces gasoline, distillate fuels, and residual fuels as primary products. Such a refinery must include equipment to convert the gasoline and distillate-fuels fractions into salable products; the principal requirements are facilities for improving the octane ratings of gasoline fractions and for "finishing" gasolines and distillate fuels by removing undesirable trace components. Such refineries are found outside the United States—in Europe, for example, where the demand for gasoline is relatively low, and the demand for low-grade fuels is high.

In the United States, gasoline and distillate fuels are usually considered the primary products; residual fuels are by-products, which may or may not be produced, depending upon the particular situation. The demand for gasoline could not be met from the supply of gasoline distilled directly from crude; higher-boiling materials must also be converted into gasoline. The heaviest fractions of crude are the hardest to convert. Whether or not they are converted depends chiefly on their values as low-grade fuels, on whether they would make satisfactory asphalts, and on the market for asphalts. In crude-oil producing areas, where natural gas is available cheaply, there is a large incentive for converting nonasphalt-type residual fuels into gasoline. In industrial areas far removed from crude-oil producing areas and coal fields, residual fuels are more valuable, and the incentive to process them is less. Therefore, the expedients used to convert heavier stocks into gasoline vary from refinery to refinery.

In the conversion of heavier stocks into gasoline, larger molecules are "cracked" into smaller ones. Some of the fragments are too small—too volatile—to be included in gasoline. These gaseous materials are usually processed under such conditions that their olefinic constituents, and some of the paraffinic as well, combine to produce more materials in the gasoline boiling range.

The most complex refineries are those which produce lubricating oils as well as gasoline and distillate fuels. Lubricating oils are usually made from high-boiling distillate fractions, although they may also be made from the residual material from the distillation of certain crude oils. A large amount of equipment is usually required for the production of lubricating oils, and wax is usually a by-product of the operations.

Until about 1950, all refineries were built with units that operated independently of each other. With this arrangement and with the provision of a large amount of tankage for intermediate products, any unit can be shut down and reconditioned independently, while the rest of the refinery continues to operate. Since about 1950, there has been a trend to integrated refineries, which are cheaper to build and to operate. In one 60,000 bbl per day refinery, integration saved 23 per cent of the investment required for an equivalent conventional refinery (1).

CHOICE OF CRUDE

What crude oils are processed at a given location depends upon a number of factors, some of which are historical. Originally a refinery site is chosen because of its proximity to petroleum fields and markets, to crude-oil and products pipe lines, or to water transportation; a source of cooling water is also a requirement. As time passes, the proximity factors may change as new petroleum fields are discovered and old ones are exhausted, and as new crude-oil or products pipe lines are built.

The processing facilities in a given refinery are designed for the optimum operation at the time each was built. Once built, the existence of any such facilities influences each subsequent decision as new possibilities arise. Thus the manner in which a refinery grew influences the direction of its future growth. Also, in large measure, it determines what petroleum crude oils are optimum for the particular refinery.

Large refineries may import several types of crudes, which may be processed separately. Crude oils that yield superior distillate fuels may be kept separate from those that produce inferior stocks. Also, crude oils that yield superior lubricating stocks or asphalts may be segregated. Such segregation does not extend usually to the operations in which heavier stocks are converted to gasoline.

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CHAPTER 3

SEPARATION PROCESSES—DISTILLATION

As it flows from the well, a petroleum oil is a dark viscous liquid whose appearance belies the sobriquet "black gold." Indeed, if it were a final product, petroleum would be merely a low-grade fuel struggling to establish itself against coal. It is its separation into simpler, more valuable products that has made petroleum the preeminent source of energy world-wide. Thus, separation processes are the backbone of refining technology. Not only are they used to obtain the primary or "virgin" petroleum products, they are also employed to recover the secondary products resulting from thermal and catalytic conversions.

The thousands of components that make up a petroleum "crude oil" differ in such physical properties as boiling point, freezing point, solubility in specific solvents, and attraction for specific solids. These differences make separation possible. The principal processes and the physical-property differences they exploit are given in Table 3-1. Other processes of lesser interest include thermal diffusion, rotary distillation, molecular distillation, gas chromatography, and clathration.

Table 3-1

Process	*Physical property*
Distillation	Boiling points
Absorption	Boiling points
Extraction	Solubilities in specific solvents
Adsorption	Attractions for specific solids
Crystallization	Freezing points

Because many of the components of crude petroleum have similar physical properties, a single process is seldom capable of separating a pure compound. Fortunately, pure compounds are seldom needed. In most cases, it is sufficient to separate a group of compounds that have similar boiling points, or freezing points, or solubilities, or attractions for solids. When a pure compound is desired, two or more successive processes are generally needed to obtain it.

DISTILLATION

The property that differentiates most petroleum products from each other is "volatility," or tendency to vaporize. More volatile products are called "lighter," less volatile products, "heavier." The volatility of a product is determined, of course, by the boiling points of its components. Inasmuch as distillation separates liquids by boiling points, distillation is the principal separation process.

Theory of Distillation

The basic principle of distillation is simple. When a solution is boiled, the lighter components vaporize preferentially and the solution is separated into a lighter overhead product and a heavier residue. For most petroleum applications, this simple operation does not suffice, and multistage units must be employed. Such units consist of cylindrical columns, or "towers," through which vapor and liquid streams pass countercurrently. Depending upon circumstances, feed may be charged at any point in the column. Products are withdrawn from the top and bottom and sometimes from intermediate points as well. Liquid withdrawn from the bottom is usually reboiled to supply vapors to the column; vapors from the top are condensed and a portion is returned as "reflux." It seems paradoxical to build complex and expensive equipment to separate out an overhead product and then to return part of it to the separation zone. Indeed, many of the technologists of the time considered refluxing foolish when it was first introduced. We may conclude from this that the function of reflux is somewhat obscure. Why it is used in a multistage unit can best be illustrated by analogy with single-stage operations.

Staging. Consider a single-stage distillation system in which a solution is heated until half of it vaporizes, the vapors then being separated from the liquid and condensed. Suppose that a two-component solution is processed in this system to concentrate the lighter component in the overhead fraction. Suppose further that the desired concentration is not attained. A more concentrated product could be obtained by charging the overhead to a second unit, and this procedure could be repeated until the desired concentration was obtained. Similarly, the heavier component could be concentrated in a bottoms cut by reprocessing successive residues. In either case, the yield of the desired product would be low, and large amounts of intermediate materials would be made. Yields could be improved by returning each intermediate material with the next charge to the preceding stage. By this means, all the original charge would be recovered ultimately in one or the other of the desired products. Such an operation is diagramed in Fig. 3-1*a*; each stage in this diagram includes equipment to vaporize a portion of the charge and to condense the vapors. Although the indicated operation is possible, equipment would be complex and expensive, and labor and energy requirements would be high. The equipment could be simplified somewhat by converting each batch stage to continuous operation as shown in Fig. 3-1*b*, but the equipment would still be complex and the operation expensive. The next step is to eliminate vaporization and condensation equipment from the intermediate steps by permitting the vapor from each stage to pass directly into the stage above, where it mixes with the liquid from the next higher stage; the contained heat in the vapor substitutes for indirect heating of the liquid. Now all that remains is to house all the intermediate steps in a single column, and we have the modern distillation unit shown in Fig. 3-1*c*.

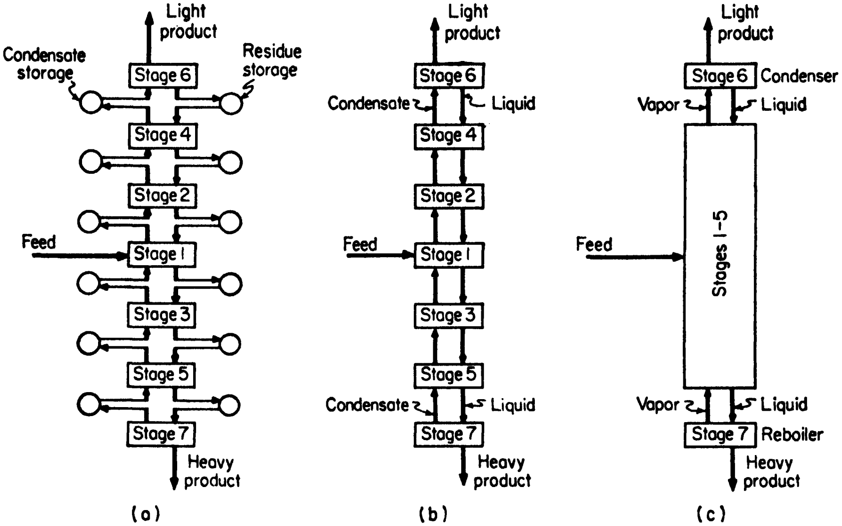

FIG. 3-1. Comparison of (*a*) batch revaporization, (*b*) continuous revaporization, and (*c*) continuous distillation.

Column Sections. The part of the column above the feed inlet is called the "rectifying section," and the part below it is called the "stripping section." The two sections have different purposes. One serves to increase the purity of a product; the other increases its recovery. In Fig. 3-1*a*, for example, stages 2, 4, and 6, which correspond to the rectifying section, increase the purity of the light product taken overhead. The liquid leaving stage 1 contains a considerable amount of the light component, and steps 3, 5, and 7, which correspond to the stripping section, strip the light component out and thereby improve its recovery in the overhead. For the heavy product, the functions of the two sections are reversed; the rectifying section improves recovery, the stripping section, purity. In some applications only one or the other of these two sections is required, depending upon the particular purity and recovery requirements of the operation.

Extractive and Azeotropic Distillation

Because distillation separates by virtue of differences in volatility, distillation cannot normally be used to separate close-boiling materials.* However, when the materials to be separated are chemically dissimilar, modified distillation procedures can be used. Examples are the separation of butenes from butanes and of toluene from *i*-octanes. In such cases, an extraneous liquid can be added which has an affinity for one of the components in the charge; as a result the relative volatilities of the original components change, and separation becomes possible (4,19,21,76). If the added material is less volatile than the original components, it is added at the top of the column and withdrawn from the bottom, and the operation is called extractive distillation. If the added material is more volatile than the original components, it is added at the top of the column or with the feed and is withdrawn in the overhead product; the operation is then called azeotropic distillation.†

Solvents and Entrainers. In extractive distillation, the extraneous liquid is called a solvent; in azeotropic distillation, it is called an entrainer. In either case, its effectiveness is determined by its concentration in the liquid phase. Consequently, the boiling point of an entrainer is limited; it must be about as volatile as the lighter feed components so that it will pass overhead, but it must not be so volatile that it will disappear from the downflowing liquid stream much above the bottom of the tower. An entrainer must be separable, of course, from the overhead product—by distillation or by some other technique. Similarly, a solvent in extractive distillation must be separable from the bottoms product. How the entrainer or the solvent is separated from the overhead or bottoms

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* Also certain materials with different boiling points cannot be separated completely by simple distillation because they form "azeotropes." The relative volatilities of chemically dissimilar materials often change as their proportions in the mixture change. With some such materials, the volatilities of the components become equal at some particular proportion; then the equilibrium vapor and liquid have the same composition, and further separation is impossible by ordinary distillation. By way of example, if a mixture of HCl and water is distilled in a batch operation, the boiling liquid will approach the same composition (20 wt per cent HCl) regardless of the initial composition. If the original solution is richer in HCl, HCl will go overhead preferentially. If it is leaner, water will go overhead preferentially. As the liquid residue approaches 20 wt per cent HCl, the overhead vapor also approaches that composition.

† The operation is called azeotropic distillation because the entrainer usually forms an azeotrope with at least one of the components in the charge.

product is an important consideration, because large volumes must be used. To be effective in changing the relative volatilities of the original components, an entrainer or a solvent must constitute at least 40 per cent of the liquid phase (60), and its concentration is usually much higher.

Effects of Reflux. In extractive distillation, reflux has two opposing effects. By increasing the counterflow of liquid and vapor, increasing the reflux promotes the separation. However, increasing the reflux lowers the concentration of the solvent in the liquid streams; this lessens its effect in spreading the volatilities of the original feed components and thus retards their separation. Because of these conflicting effects, there is apt to be a sharp optimum in the reflux rate for an extractive-distillation operation.

Feed Preparation. Only narrow-boiling materials are charged to extractive or azeotropic distillation. The reason may be seen most readily from an example. Consider extractive distillation for the separation of toluene from a mixture with *i*-octanes, which normally boil very closely to toluene. Lower-boiling materials (like hexane and benzene) and higher-boiling materials (like *i*-nonanes) are first separated by ordinary distillation. The sharpness of removing the light ends affects only the amount of material charged to extractive distillation. On the other hand, the purity of the toluene product will depend upon the sharpness of prefractionating the heavy ends out of the feed.

How poor removal of heavy ends affects product purity may be seen by considering the normal volatilities of the feed components and how they are affected by the presence of a solvent. Toluene and *i*-octane boil together, and *i*-nonanes are about half as volatile. In the concentrations usually employed, a solvent approximately doubles the volatilities of the paraffins relative to toluene. In the presence of the solvent, then, the *i*-nonanes have about the same volatility as toluene, and their separation is very difficult, and sometimes impossible.

Even when heavy materials can be taken overhead in extractive distillation, they may be very undesirable in the feed. When phenol is used as the solvent, for example, volatility relationships are such that heavy paraffins in the overhead tend to carry some phenol with them (19). Phenol is expensive, and only small losses can be tolerated.

Commercial Distillation Equipment

A commercial distillation unit requires considerable equipment in addition to the column proper—a condenser for the overhead vapors, a reflux drum to receive condensate, a reboiler to partially vaporize the bottom liquid, pumps to charge feed and reflux and to withdraw products, and automatic control equipment. However, the column is the heart of the unit. Its function is to facilitate transfer of materials between the counterflowing streams—light materials from the liquid to the vapor, and heavy materials from the vapor to the liquid. To promote such transfers, a commercial column is equipped with internal "trays" or "packing" to facilitate contacting of the liquid and vapor streams.

Trays. "Trays" are horizontal contacting devices usually spaced 1 to 3 ft apart. How they function is illustrated in Fig. 3-2. Liquid reflux, discharged onto one side of the top tray, flows across it and over a weir to a "downcomer" that directs it to the next lower tray. The process is repeated on each successive tray until the liquid reaches the bottom. Vapors from the bottom of the column pass up through openings in each tray and through each cross-flowing liquid until they reach the top. Some columns dispense with weirs, and some with downcomers also. When downcomers are not provided, the liquid and vapor pass countercurrently through the same tray openings.

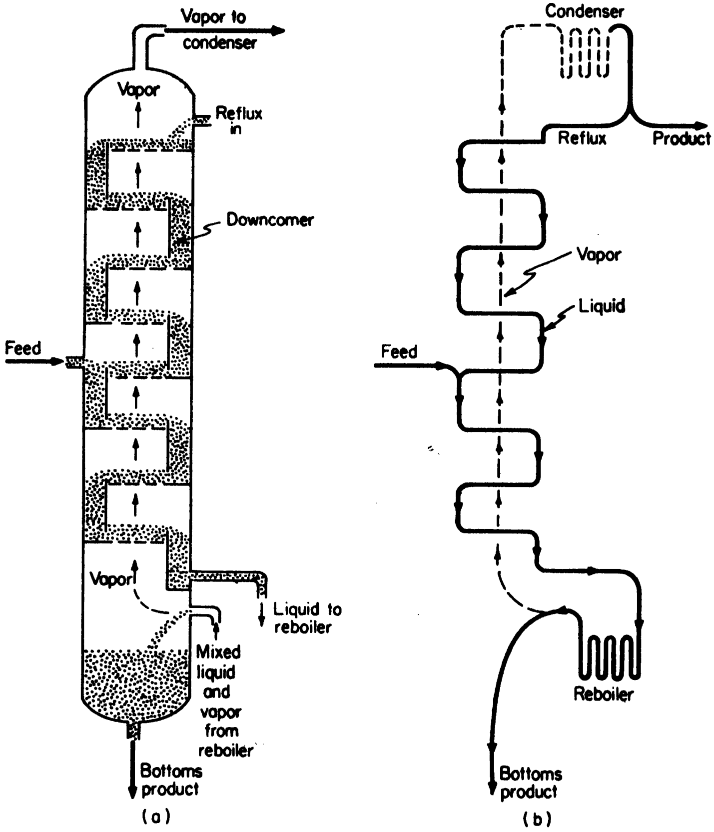

FIG. 3-2. Operation of a tray-type distillation column. (*a*) Typical tray column. (*b*) Flow of liquids and vapors.

At least eight types of trays (or "plates") are in commercial use. In petroleum refining, bubble-cap trays have long been dominant. Sieve trays, which are popular in the chemical industries, have also achieved some stature in petroleum refining (23). Also, a number of other trays have been developed that are claimed to be better and cheaper than bubble trays. These include Flexitrays, float-valve trays, Uniflux trays, Kascade trays, Turbogrids, and ripple trays. Because they are among the simplest of the common trays, sieve trays will be discussed first.

Sieve Trays. Sieve trays are horizontal plates perforated in a regular pattern—typically, $\frac{3}{16}$-in. holes on $\frac{1}{2}$-inch square centers (61) or $\frac{1}{8}$-inch holes on $\frac{3}{8}$-inch triangular centers (40). The term "perforated tray" is usually used interchangeably with sieve tray, but it sometimes means a high-capacity tray with smaller, more closely spaced holes—$\frac{3}{32}$-in. holes on $\frac{3}{16}$-in. centers, for example (24). In comparison with other sieve trays, the latter arrangement permits the use of smaller-diameter towers, but more height is required.

Use of sieve trays has been retarded by an impression that their operating range is limited (61); however, recent data indicate that, when properly designed, their operating range is as wide as that of other types (40,49).

A problem peculiar to sieve trays is the need to install them horizontally. If a tray is so installed, the rising vapors prevent liquid from passing through the perforations; however, if the tray is tilted, liquid may pass through the lower holes and thus bypass all or part of the tray. Because there is a hydraulic gradient from the liquid inlet to the outlet of a tray, a slight tilt downward in the direction of liquid travel is not objectionable, and such a tilt is sometimes specified to ensure against an inadvertent tilt in the opposite direction (49).

Corrosion is a greater problem with sieve trays than with others because it changes the size of the perforations and thus changes the operating characteristics of the trays.

Bubble-cap Trays. Bubble-cap trays differ from sieve trays in that the holes are fewer but larger, each hole is equipped with a chimney or "riser," and each riser is capped by a bubble cap. As shown in Fig. 3-3, vapors pass up through the risers, are directed downward into the cross-flowing liquid by the bubble caps, and then rise through the liquid, carrying some droplets with them. Bubble caps are either round bell caps with diameters of 4 to 7 in. or rectangular caps 3 to 6 in. wide and 12 in. or more long. Their lower walls are slotted to permit passage of vapor, and they are usually spaced 1 to 3 in. apart. Bubble-cap trays are more expensive than sieve trays, but levelness of installation is not critical, and corrosion does not affect their operating characteristics as much. The bubble-cap design is the patriarch of all trays, having been used as early as 1813 (27).

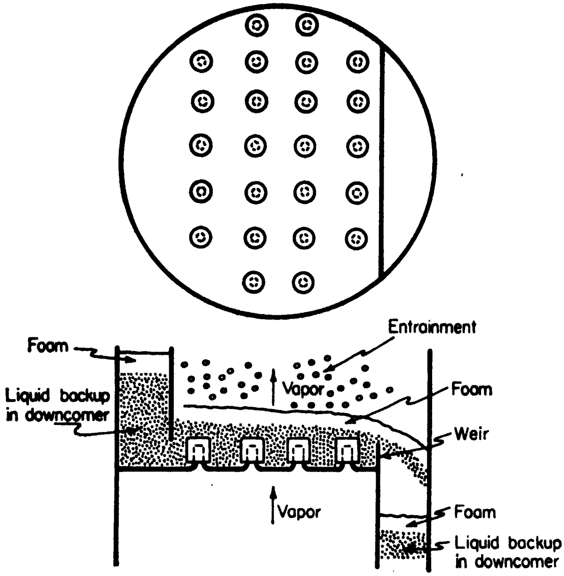

FIG. 3-3. Operation of a bubble-cap tray. Bubble caps are spaced more closely than indicated in the sketch.

Flexitrays and Float-valve Trays. Flexitrays (75) and float-valve trays (55) combine some of the better features of sieve and bubble-cap designs. Both are flat trays with relatively large holes or slots, each of which has a flat cover plate that is free to move vertically. The cover plates are raised by the rising vapors, the amount of opening increasing with the vapor flow rate. Both Flexitrays and float-valve trays are cheaper than bubble-cap trays and both avoid the installation and corrosion problems of sieve trays. They are also claimed to be more efficient* and to have greater capacities than bubble-cap trays.

Uniflux Trays. Uniflux trays (7) operate on the same general principle as bubble-cap trays, but they are simpler and cheaper to build and maintain. As shown in Fig. 3-4, they are made up of square-S cross members fitted together in such a way as to form long, narrow, rectangular risers connected to parallel vapor passages, also long and narrow, that direct the vapors down into the cross-flowing liquid. Each riser and vapor passage extends across the tower, transverse to the flow of liquid.

Kascade Trays. Kascade trays are also shown in Fig. 3-4. They are similar to Uniflux trays, except that each S member is shallower and each successive member (in the direction of liquid flow) is lower than the preceding one. Also, each member is provided with a weir, the upper

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* Tray efficiency refers to the ability of a tray to promote transfer of materials between the liquid and vapor phases.

part of which is perforated. A later version, the horizontal Benturi, is also shown. Benturi trays are claimed to have high efficiencies, high capacities, and low pressure drops (74).

Turbogrids. A Turbogrid tray (63) is the simplest of trays. Consisting of a grid of parallel slots, it is made either by stamping slots out of a flat metal plate or by the use of parallel bars. Downcomers are usually not provided, and then the liquid and vapor pass through the same openings, the interference of the counterflowing streams causing the desired head of liquid to be built up on each tray. Turbogrids are cheaper than bubble-cap trays and are claimed to have more capacity, but their operating range is narrower.

Ripple Trays. A ripple tray (39) is a sinusoidally corrugated tray perforated with ⅛ to ⅜-in. holes to give an open area of 15 to 30 per cent of the total cross-sectional area. As with Turbogrids, downcomers are not used and the interference of the counterflowing streams causes a liquid level to be built up on the tray. Liquid tends to pass through the holes in the "valleys," vapor through the holes in the "hills." The trays are claimed to be low cost, with high capacities and efficiencies. They are also claimed to be particularly useful in dirty services, for example, when solids are present or when the feed stock tends to polymerize to carbonaceous solids ("coke") on the trays. One-eighth-inch holes are used in clean services, larger holes in dirty services.

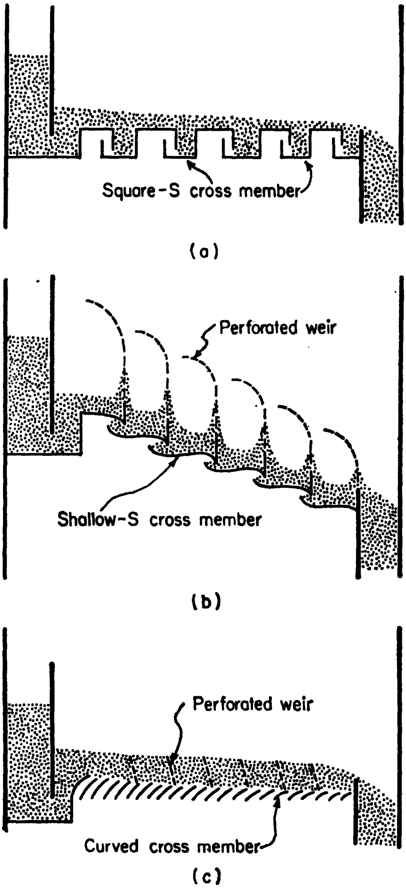

FIG. 3-4. Types of trays. (*a*) Uniflux tray. (*b*) Kascade tray. (*c*) Benturi tray.

Tray Comparisons. A realistic comparison of the performance of competing trays is not possible from published information. For the most part, published data are incomplete and seldom for the same operations. Some attempts at comparison have been made, of which Table 3-2 (41) is typical. At the present state of the art, such comparisons must be considered only tentative because the newer trays are usually compared with well-designed bubble-cap trays, and there is no common standard for such trays. By way of illustration, it is claimed that, in the six-year period from 1948 to 1954, the capacities of well-designed bubble-cap trays increased 60 per cent, while contacting efficiency improved 30 per cent (78). Nevertheless, it does seem likely that one or more of the newer trays will supplant bubble-cap trays, at least in new installations.

Table 3-2

Tray description	Contacting efficiency	Relative capacity	Relative cost	Pressure drop
Bubble cap	Good	1.0	1.0	Moderate
Uniflux	Good	1.0	0.4–0.6	Moderate
Flexitrays	Good	1.1–1.5	0.6–0.8	Moderate
Turbogrid	Good	Up to 1.5	0.4–0.7	Low
Sieve	Good	1.1–1.4	0.6–0.7	Low

Packings. Packings consist of loose pieces of solid material that fill the column except for short spaces at the top and bottom. By providing surface over which the downflowing liquid distributes itself, they increase the area of contact between liquid and vapor and thus promote the transfer of materials between the two streams. Raschig rings have been the most popular packing. They are small, hollow cylinders open at both ends, with length equal to diameter. Packed distillation columns are used in petroleum refining only in special situations—for small-diameter columns or where materials corrosive to metals are distilled. Packings are used in small-diameter columns because maintenance of small tray columns is difficult. When corrosive materials are distilled, nonmetallic packings are often used.

Other packings include Panapak, which has a high capacity (73), Stedman and protruded-metal packings, which have high efficiencies (9,62), and Goodloe packing, which has intermediate characteristics (10).

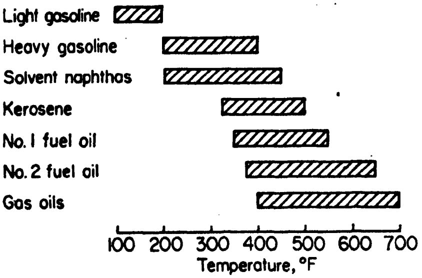

FIG. 3-5. Distillate products obtainable by atmospheric distillation of crude oil.

Distillation Operations

Although all distillation operations are based on the same principles, there are considerable differences in the equipment provided for different applications. However, most petroleum distillations fall into three broad categories: atmospheric distillations of crude oils, vacuum distillations, and reboiled distillations. Azeotropic and extractive distillations are also carried out to a limited extent.

Crude Distillation. The first major operation in the refining of petroleum is distillation at atmospheric pressure. The various possible products overlap each other, as shown in Fig. 3-5. How best to cut up a crude oil in each instance depends upon the properties of the crude, the market of the individual refiner, and the characteristics of the other processing equipment in the refinery, for example, whether the refinery includes facilities for manufacturing lubricating oils. The refiner must choose which products to maximize. Some typical operations are shown in Table 3-3.

Table 3-3. Typical Material Balances for Crude Distillation

	Vol % of crude oil			
	Mid-Continent	West Texas	Pennsylvania	Oklahoma City
Light gasoline	27	16	17	20
Heavy gasoline	5	15	20	4
Kerosene or heater oil	14	14	11	12
Gas oil	13	14	16	20
Paraffin distillate[a]	18	...	19	14
Heavy wax distillate	...	...	...	7
Residue	23	41	17	23

[a] Light lubricating-oil fraction, containing paraffin wax.

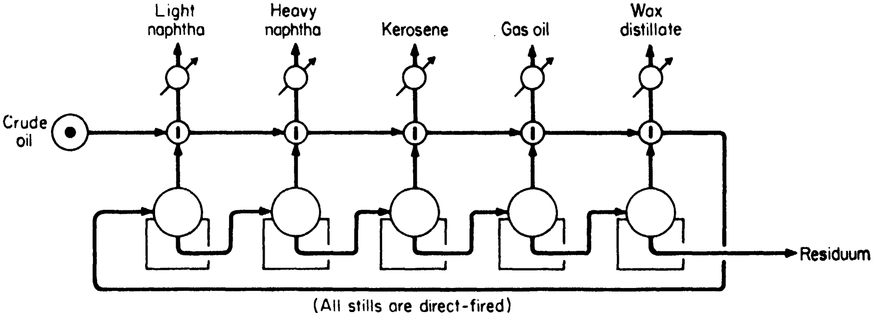

FIG. 3-6. Battery of shell stills.

In older units, crude distillation is accomplished in a battery of "shell stills," as shown in Fig. 3-6. Preheated crude is charged continuously to horizontal, cylindrical stills, externally fired. The lightest cut is taken off at the first still, and the remaining liquid passes on to the following stills, where the process is repeated, successively higher-boiling cuts being obtained at each still. Most shell stills are equipped with short bubble-cap columns to improve separation. Shell stills have been almost completely supplanted by "pipe stills," which are cheaper to build and to operate.

A modern pipe still is illustrated in Fig. 3-7. In this unit, the heat for vaporization is supplied by heating the whole crude in a furnace. Preheated crude is charged into the bottom of a distillation column at a pressure slightly above atmospheric, and the vapors rise through the column, contacting a downflowing reflux stream; as a result, the lightest materials concentrate at the top of the column, the heaviest materials at the bottom, and intermediate materials in-between. Desired products are withdrawn at appropriate points. Because the lighter products (as vapor) must pass through the heavier products (as liquid) and must be in equilibrium with them at each point in the column, each sidestream contains some light ends. As indicated in the figure, steam strippers are sometimes used to eliminate light ends from a sidestream. The sidestream is fed to the top of the stripper; countercurrent steam strips out the light ends and carries them back into the main column. Although steam may also be used at the base of the main column to strip the residue, pipe stills are primarily rectifying columns; if steam is employed for stripping the residue, only a few trays are so employed.

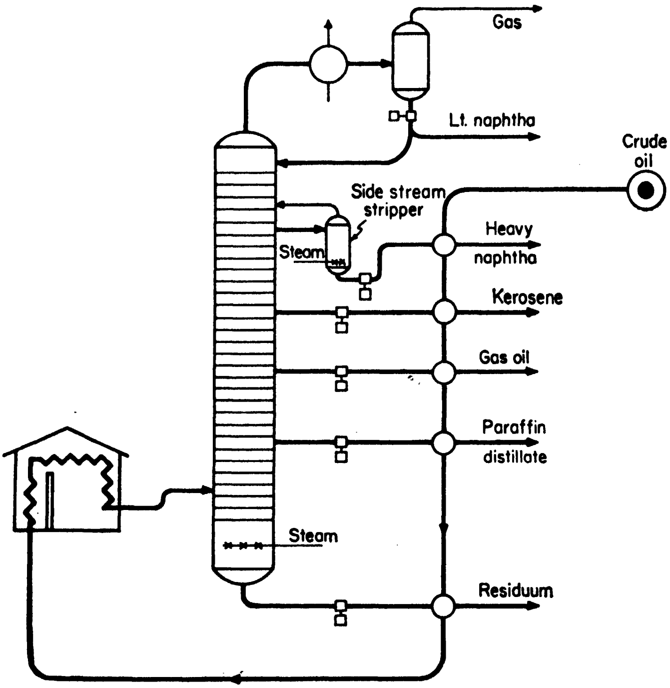

FIG. 3-7. Pipe-still crude-distillation unit.

Temperature is a limiting factor in the operation of crude-distillation units. There are two limitations: (1) high temperatures may cause degradation of valuable stocks, such as lubricating oils, and (2) high temperatures may cause furnace tubes to coke up rapidly. The maximum temperature that can be used depends upon the stability of the crude, the product requirements, and the design of the distillation equipment. Table 3-4 gives a typical temperature pattern.

Table 3-4

Operation	*Temperature, °F*
Light gasoline take-off	240
Heavy gasoline draw-off	335
Kerosene draw-off	420
Gas-oil draw-off	500
Light wax-distillate draw-off	600
Bottoms draw-off	800

Vacuum Distillations. Some materials are too high boiling or too heat sensitive to be distilled at atmospheric pressure. Because boiling points go down as the pressure is lowered, such materials can often be distilled under vacuum. In the petroleum industry, vacuum distillation is used in the production of lubricating oils, asphalts, and charge stocks to catalytic cracking.* All these operations are similar in that a "topped" crude (the bottoms from an atmospheric-pressure distillation) is distilled in a column operating under a vacuum. The cuts taken overhead depend upon the purpose of the operation, as well as on the sensitivity of the stocks and the design of the distillation equipment. Typical preheater outlet temperatures are (53,3):

For production of lubricating oil	730°F
For production of asphalt	770°–815°F
For production of cracking charge	850°F

Pressures are usually between 30 and 80 mm Hg absolute, although lower pressures have been employed (1). Steam is used to reduce the hydrocarbon partial pressure further; steam usage may range from 1.5 to 15 lb per bbl of reduced crude processed (5).

Vacuum distillation units are very similar to atmospheric crude-distillation units, except that the large vapor volumes at lower pressures require that columns be much larger; vacuum columns as large as 40 ft in diameter are in operation. Equipment must be supplied to maintain the desired vacuum; steam jets and a barometric condenser are usually used (58).

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* Charge stocks to catalytic cracking are usually distillates, and asphalts are always residues. Lubricating oils are usually distillates, although residues from some crudes are also used.

Reboiled Distillations. Inasmuch as the fractionating columns in crude-distillation units and in vacuum units are rectifying columns primarily, considerable amounts of light materials are left in the bottoms. In most refinery applications, such an operation would not be satisfactory; both a rectifying and a stripping section are usually needed to obtain an adequate separation. Accordingly, the feed is charged to an intermediate point in the column, and heat for vaporization is supplied by withdrawing a bottoms fraction, partially vaporizing it in a reboiler, and then returning it to the column. A typical two-column unit is illustrated in Fig. 3-8. Designed to prepare feed stock for a pentane-hexane isomerization unit and a catalytic reforming unit, the two columns separated a virgin gasoline charge into five fractions. Butanes were taken overhead from the first column, isomerization feed as a sidestream. The bottoms were processed in the second column to yield an intermediate overhead stream, feed for a catalytic reformer as a sidestream, and heavy-gasoline bottoms.

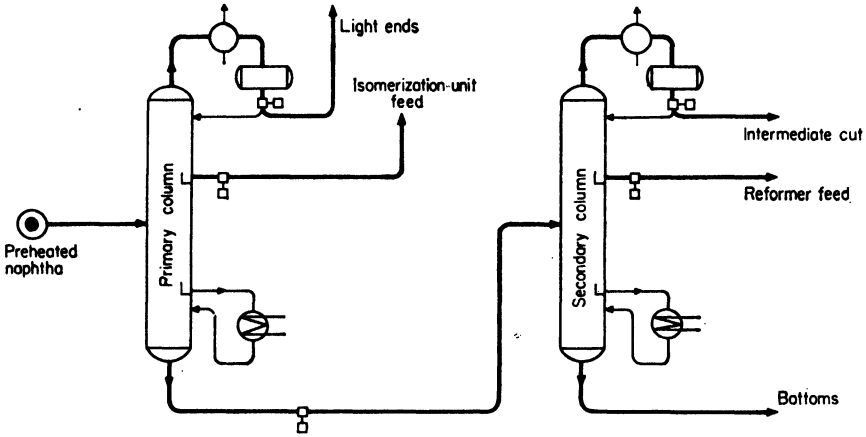

FIG. 3-8. Schematic diagram of a reboiled distillation unit.

A heavy sidestream is sometimes withdrawn as vapor from a point below the feed inlet (54), but the operation is not common.

Interesting applications of distillation are in the recovery of ethylene from gases and in the separation of ethyl benzene from xylenes. In ethylene operations, very low temperatures are required, and refrigerant temperatures as low as −155°F are used commercially (67). Ethyl benzene boils only about 4°F below the xylenes; consequently more than 300 trays are used to separate it (12). For mechanical reasons, the ethyl benzene column is broken down into three sections, each 200 ft high.

Extractive and Azeotropic Distillations. Extractive and azeotropic distillations are used to separate materials in the gasoline boiling range from mixtures. Extractive distillation is used to separate butenes (34,70), butadiene (32,51,70), and individual aromatics such as benzene (65) and toluene (19). Azeotropic distillation is used in making high-purity benzene (8) and high-purity toluene (28,42).

Illustrated in Fig. 3-9 is an extractive distillation unit for the production of toluene. A wide-boiling charge stock (from catalytic reforming) is fed to a two-column fractionation system. Hexanes and lighter materials are taken overhead in the first column, and the bottoms are charged to the second. There, a narrow-boiling toluene concentrate is taken overhead and heavy ends are discharged as bottoms. Toluene concentrate is charged to the middle of an extractive-distillation column, where it is distilled in the presence of a downflowing phenol stream. A paraffinic "raffinate" passes overhead as a vapor. From the bottom of the column a phenol-toluene stream is taken to a solvent-stripping column, where the toluene product is fractionated from the phenol. Phenol recirculates to the extractive-distillation column to complete the cycle. The paraffinic overhead from the extractive-distillation column contains some phenol, which is separated from the raffinate in a solvent-recovery column. In some units, the extractive-distillation column is extended to include a solvent-recovery section, and a separate solvent-recovery column is not provided.

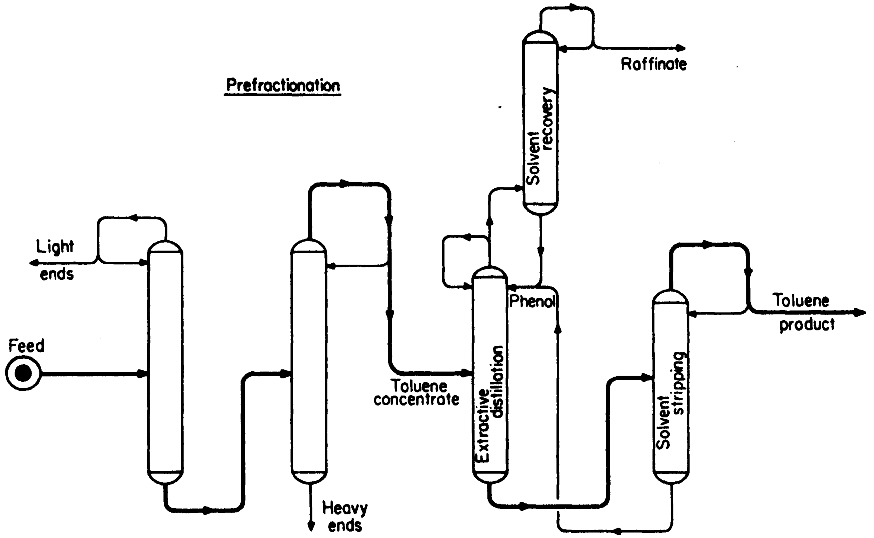

FIG. 3-9. Extractive-distillation unit for producing high-purity toluene.

As shown in Fig. 3-10, azeotropic distillation is also used for the recovery of toluene (42). As in extractive distillation, the feed stock is first prefractionated in a two-column system to obtain a narrow-boiling heart-cut, which is then fractionated in the "azeotroping column" in the presence of about three volumes of methylethylketone (MEK)-water entrainer per volume of nonaromatics in the feed, and with a reflux/overhead product ratio of 2:1. The nonaromatics pass overhead with the MEK water, and 99 per cent toluene is taken off as bottoms. The overhead stream passes to an extraction column, where the MEK is extracted from the hydrocarbons by water. Dilute MEK from this operation is then fractionated to concentrate it to the desired level for recycling to the azeotroping column. To minimize losses of MEK in the raffinate and extract streams, both are fractionated (in towers not shown) to take overhead any MEK, together with a small amount of hydrocarbons. The toluene–MEK stream is recycled directly to the azeotropic-distillation column. The overhead from topping the raffinate is extracted with water, and the two resulting streams (both small) are blended with the corresponding streams from the main extractor. In commercial operations, toluene recoveries of 95 to 98 per cent are obtained.

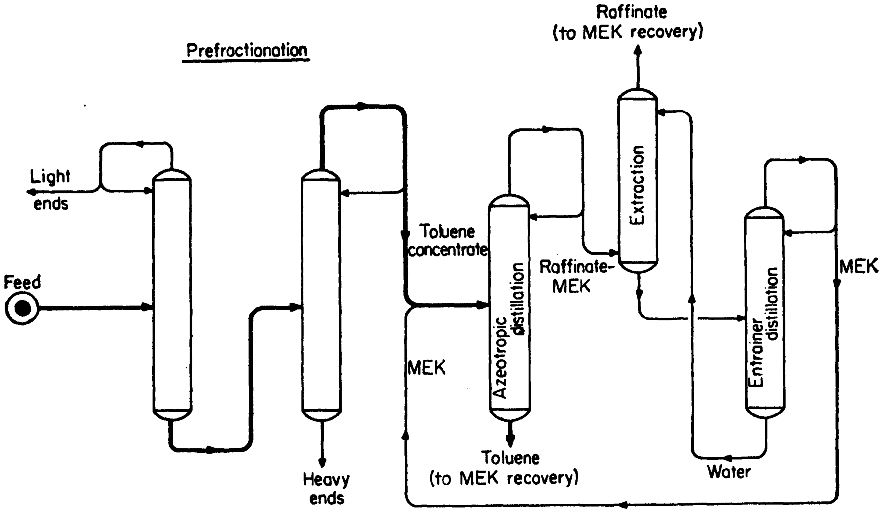

FIG. 3-10. Azeotropic-distillation unit for producing high-purity toluene.

If nitration-grade toluene is to be made, the toluene product is acid treated and refractionated to remove traces of unsaturated materials.

Laboratory Distillations

To provide basic data for design and to characterize products, three types of laboratory distillations are in common use: the true boiling point, the ASTM, and the equilibrium-flash distillation.

True-boiling-point Distillation. A true boiling point (or TBP) distillation separates the solution almost completely into its components.

Separation is accomplished by the use of a large number of equilibrium stages* and a large amount of reflux, for example, 100 equilibrium stages and 100 volumes of reflux per volume of overhead product. Because products are taken overhead essentially pure, the top temperature of the column remains constant until the lowest-boiling component is completely removed; the temperature then rises sharply to the boiling temperature of the next-lowest-boiling material and remains there until that component is exhausted, and this step is repeated until the distillation has been completed. A TBP apparatus and a TBP curve for a binary system are illustrated in Fig. 3-11*a*. Obtaining a TBP curve is expensive and time-consuming; consequently TBP tests are not employed on a routine basis.

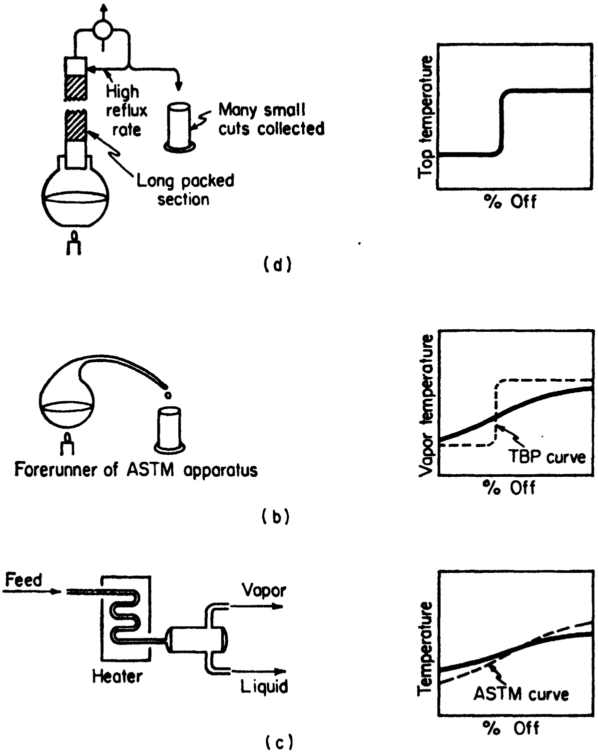

FIG. 3-11. Laboratory distillations (two-component feed). (*a*) TBP distillation. The distillation is carried out in such a way that the components are almost completely separated from each other. (*b*) ASTM distillation with no column and no intentional reflux, and with the vapor separated as it is formed. (*c*) EFV distillation with no column and no reflux; vapors not separated until desired vaporization is achieved.

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* An equilibrium stage is an apparatus (or a section of a column) such that the vapor and liquid leaving it are in equilibrium.

A typical TBP curve for a gasoline product is illustrated in Fig. 3-12*a*. Initially, the temperature goes up in well-defined steps, each step representing a single component (*i*-butane, normal butane, *i*-pentane, etc.). As the boiling temperature (and the size of the molecules) increases, the number of close-boiling isomers increases, and the steps become less distinct. Consequently the steps become smaller and smaller, until they merge into a smooth curve.

ASTM Distillation. ASTM distillations are carried out in a simple apparatus designed to boil the test liquid and to condense the vapors as they are generated. Vapor temperatures are noted as the distillation proceeds, and they are plotted against "per cent off," or the amount taken overhead.* Because only one equilibrium stage is used, and no reflux is intentionally returned (although a small amount does condense on cool surfaces and drop back into the boiling liquid), the separation is poor, and mixtures pass overhead. Therefore, the initial boiling point of an ASTM distillation is higher, and the end point is lower than the corresponding points in a TBP distillation of the same liquid. An early forerunner of the ASTM apparatus and a typical ASTM curve for a binary system are shown in Fig. 3-11*b*. The TBP curve for the same system is shown for comparison. ASTM distillations are employed as routine tests.

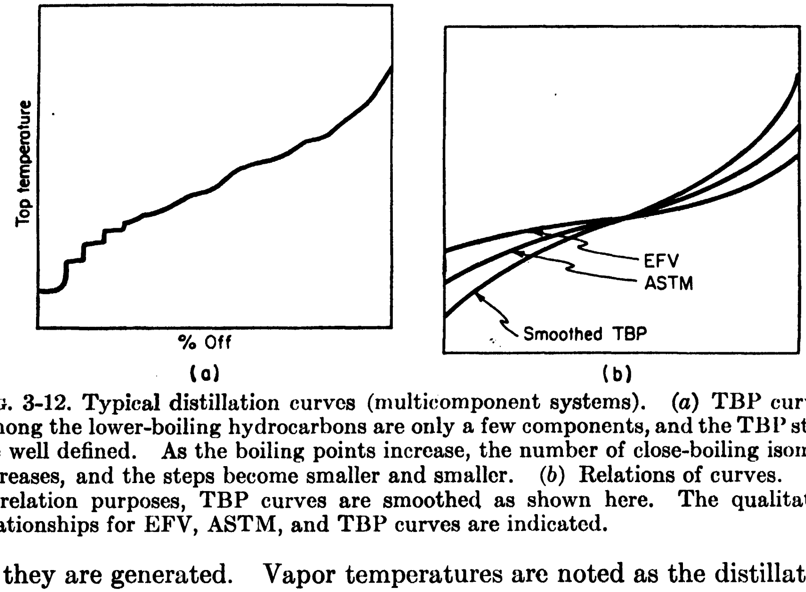

FIG. 3-12. Typical distillation curves (multicomponent systems). (*a*) TBP curves. Among the lower-boiling hydrocarbons are only a few components, and the TBP steps are well defined. As the boiling points increase, the number of close-boiling isomers increases, and the steps become smaller and smaller. (*b*) Relations of curves. For correlation purposes, TBP curves are smoothed as shown here. The qualitative relationships for EFV, ASTM, and TBP curves are indicated.

Equilibrium-flash Distillation. Equilibrium-flash-vaporization (EFV) operations are similar in principle to ASTM distillations, except that the

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* Sometimes, the results are expressed as "per cent evaporated," which is equal to "per cent off" plus any distillation losses.

vapor and liquid are kept in contact until the desired degree of vaporization is reached. As a consequence, the separation is poorer than the ASTM separation. To establish a curve, several runs are needed, with each run determining a point. A schematic equipment diagram and a typical EFV distillation curve are shown in Fig. 3-11*c*. An ASTM curve for the same system is also shown for comparison. EFV curves are obtained to provide design data.

Correlations. Empirical correlations relate the TBP, ASTM, and EFV curves for a hydrocarbon mixture. The relationships for a typical multicomponent system are shown in Fig. 3-12*b*. Any one of the three curves may be estimated from either of the other two (22). At subatmospheric pressures, the correlations are subject to considerable uncertainty (26). For correlation purposes, TBP curves are smoothed.

Design of Distillation Equipment

Design of distillation equipment involves four distinct steps. First, the designer must decide how sharp the separation should be. Next, the pressure and temperatures of operation must be chosen, and the tray and reflux requirements must be determined, either on the basis of experience or of fundamental calculations. Finally, equipment must be sized. A straightforward solution along these lines is possible whenever there is no question as to how good the separation should be. Frequently, however, the optimum degree of separation depends upon investment and operating costs, and these depend, in turn, upon the design. In such cases, several solutions may be needed to determine the optimum.

Criteria of Separation. In deciding how sharp a separation should be, there are two problems: determining the degree of separation desired and translating it into terms that can be used in a distillation calculation. With light hydrocarbons, neither of these is difficult; the separation can be specified by how two components split between, for example, the overhead and bottoms products. Setting the criteria for heavier hydrocarbons is more difficult because the individual components boil closely together and because the specification to be met is usually not related directly to the fractionation calculations. By way of example, a kerosene might be distilled to meet a flash specification; this specification cannot be used directly, but must be translated into a distillation characteristic that can be used as a basis for design.

Pressure and Temperatures. Pressure and temperatures are the first operating conditions to be set. They are related; the higher the pressure, the higher the temperatures. Because crude-running units are limited by the temperature at which cracking commences, they are designed to operate at atmospheric pressure. Because the cost of vacuum equipment increases as the pressure is lowered, vacuum units are designed to operate as close to atmospheric pressure as possible, thus at the maximum permissible temperature. For reboiled columns, a range of pressures is possible, and the designer attempts to choose the economic optimum. The pressure of a reboiled column must be high enough to permit reflux to be condensed by heat exchange with the available cooling medium, but low enough that the bottoms product can be reboiled by heat exchange with the available heating medium. Care must also be taken that the pressure is low enough to avoid overheating the bottoms product or exceeding its critical temperature.* In selecting a pressure within the acceptable range, three effects should be considered: the effects on the cost of the column, on the cost of the heat-exchange equipment, and on the heat requirement for the operation.

Pressure affects the cost of the column in several ways. First, vapor-handling capacity increases with pressure; therefore, for a given flow of vapor, a smaller diameter may be used when the pressure is higher. Second, the higher temperatures that accompany higher pressures reduce driving forces for the separation, but improve the approach to equilibrium on each tray. Because the reduction in driving force is usually the more important, increasing pressure usually increases tray or reflux requirements. Finally, the thickness of the tower shell varies directly with pressure and with tower diameter. How the capacity of a debutanizing column changed with pressure was determined by tests in the field (13). The pressure for maximum capacity changed with the separation desired, ranging from about 70 psia to about 140 psia. Within 20 psi of the optimum pressure in each case, the effect of pressure on capacity was small. In view of this fact, and because reflux requirements increase with pressure, the optimum design pressure should be lower than the pressure for maximum capacity. Atkins and Wilson state that "it is usually economical to select the lowest operating pressure which will still permit satisfactory condensation of the distillate and the reflux at normal cooling-water temperatures" (2).

As the operating pressure increases, all the column temperatures go up. Thus, raising the pressure increases the driving force for transferring heat of condensation to the cooling medium, but it reduces the driving force for reboiling the bottoms. As a consequence, the size of the condenser is reduced and the size of the reboiler is increased as the pressure goes up.

Because temperatures are higher at higher pressures, more sensible heat must be supplied to the feed for a higher-pressure operation.

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* The critical temperature of any fluid is the temperature above which it cannot be liquefied at any pressure. Critical temperatures can be estimated from boiling points (29,46).

Although a part of this heat can be recovered by heat exchange of the products with the feed, sensible-heat requirements increase with pressure.

Reflux and Trays. The sharpness of any separation depends upon the volatilities of the feed components, the amount of reflux employed, and the number of trays or the amount of packing provided in each section of the column. Where past practice is an adequate criterion for design, empirical relationships are used for specifying reflux and tray or packing requirements. This approach is used generally for designing crude-distillation units, primary fractionators in cracking units, and similar columns. Most of the columns handling light hydrocarbons are designed from fundamental considerations.

In crude-distillation units, reflux cannot be varied at will. Because all the heat is brought in with the feed, the vapor rate is limited by the maximum temperature to which the crude can be heated. It is usually economical to take off as distillates as much of the charge as is possible. Also, the sharpness of separation between the heaviest distillate and the bottoms is not of much concern. For these reasons, crude-distillation units are operated to return little reflux to the feed zone. Because the temperature and the molecular weight of the rising vapors drop as the vapors pass up the column, the liquid reflux, on a molal basis, increases. Fortunately this trend parallels the fractionation requirements, the lower-boiling products requiring sharper fractionation. Usually there is more reflux than needed in the upper part of the column, and reflux in that section is often reduced deliberately by withdrawing a liquid stream at an intermediate point in the column, cooling it, and returning it to the tower. The liquid and vapor streams above this point are thus reduced, and a smaller column can be used. The design problem in crude distillation is primarily one of determining the number of trays. Tray requirements are usually estimated empirically (59), but they can be obtained from fundamental considerations (66). Typically a crude-oil fractionator may have the following requirements (48):

Between light and heavy gasoline draw-offs	6–8 trays
Between heavy gasoline and kerosene draw-offs	5–6 trays
Between kerosene and gas-oil draw-offs	4–7 trays
Between gas-oil draw-off and feed inlet	3–4 trays
Below the feed inlet	4–6 trays
In sidestream strippers	4–5 trays

Vacuum columns are designed in the same way as crude-oil fractionators, except that care is taken to minimize pressure drop and entrainment and to avoid coking on the trays (2,5). One or more distillate products may be made, and only a few trays are employed—usually from one to five between products (48), although as many as eight are sometimes used. Minimizing pressure drop is important because vacuum is applied to the top of a column (or to the reflux drum) to reduce pressure at the bottom, and pressure drop in the column increases the pull required of the vacuum equipment. One way to minimize pressure drop is to provide a few heat-transfer trays at the top of the column to condense most of the hydrocarbons. Liquid is pumped from the lowest of these trays through a cooler and back to the top of the column. Pressure drop on the heat-transfer trays is lower than it would be in a condenser to do the same job. Also, if jet condensers are used to pull the vacuum, the use of heat-transfer trays minimizes oil contamination of the steam condensate.

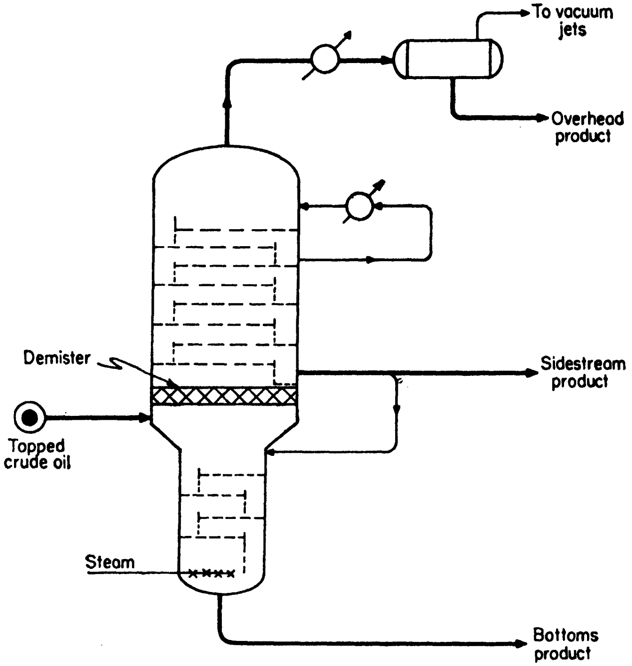

FIG. 3-13. Vacuum column design.

Entrainment is a particular problem in vacuum distillation because of the high vapor velocities encountered at low pressures. Entrainment of residual liquid into the products can be minimized by the use of wire-mesh demister pads just above the feed inlet, or by the use of two refluxed bubble trays below the lowest product-draw-off tray (2). Tangential introduction of feed to the column also helps (5), and a centrifugal separation device is sometimes used (33). Demisters coke up in use and are periodically replaced. Coking may be alleviated by continuous washing of the demister with a gas-oil stream, which is recirculated over the demister pad (57), but washing is not always effective (64).

In conjunction with charging the feed through a centrifugal separation device, a light-oil spray may be used below the pad to saturate the upflowing vapor and ensure that the pad operates wet (33). The operation of a vacuum unit that includes a demister pad is shown schematically in Fig. 3-13.

For light-hydrocarbon distillation units (such as depropanizers, debutanizers, pentane splitters, etc.) reflux and theoretical-plate* requirements are usually determined from fundamental calculations. The calculations are made stepwise from theoretical plate to theoretical plate by means of heat and material balances and of vapor-liquid equilibria data (11,16,30,45,77). For binary systems, the calculations are simple (50,36) and the multicomponent systems usually encountered in petroleum refining are solved most readily by treating them as equivalent binary systems (35). The same procedure has been used for extractive distillation (20). Theoretical-plate requirements are also determined by machine computations (69).

Qualitatively, the relationship between reflux and theoretical plates is shown in Fig. 3-14. The minimum reflux (72) is the reflux required with an infinite number of stages. Minimum plates (25) are obtained as the reflux rate approaches infinity. A popular rule of thumb is to use 1.5 times the minimum reflux and 1.8 times the minimum plates. This relationship is taken from an empirical correlation of reflux and plate requirements (31).

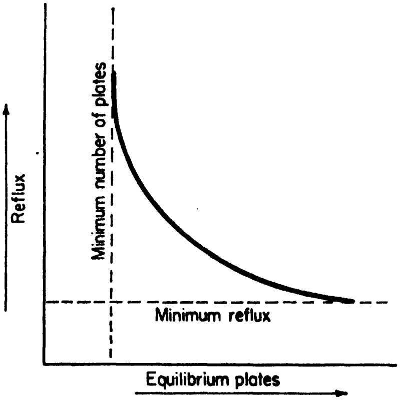

FIG. 3-14. Reflux and theoretical-plate requirements.

If bubble-cap trays are used, actual tray requirements are usually estimated by means of empirical correlations of "tray efficiency" against the properties of the refluxing liquid (18,56). Tray efficiency represents the approach of an actual tray to a theoretical plate.† Tray efficiencies are also affected by the tray details, and these are sometimes taken into account (6*a*).

Column Height and Diameter. With the number of trays set, column height is determined by the spacing of the trays, which is in turn a function of diameter and of tray details. Thus, height and diameter are

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* A theoretical plate is a section of the column such that the vapor and liquid leaving it are in equilibrium.

† $\text{Tray efficiency} = \dfrac{\text{number of theoretical plates}}{\text{number of actual trays}} \times 100$

determined together. Generalized sizing correlations have been published only for sieve (37,38,43) and for bubble-cap trays (6). For other trays, capacities are usually described relative to bubble-cap trays, although preliminary correlations have been proposed for Benturi trays (74).

The original methods for sizing bubble-cap columns considered only vapor-handling capacity. As a consequence, columns were frequently limited by liquid-handling capacity. In the sizing of modern units, both the vapor and the liquid loads are taken into account. The various methods that have been published relate tray spacing to the pressure drop across a tray. Liquid flowing from a tray to the next lower one must counterbalance this pressure drop; consequently, a head of liquid is held up in the downcomer. This head must be less than the tray spacing; if it is not, liquid fills the spaces between the trays and the tower "floods." In setting tray spacing, possible foaming of the liquid must be provided for. Accordingly, the design backup, calculated on the basis of no foaming, is usually set at about 50 per cent of the tray spacing.

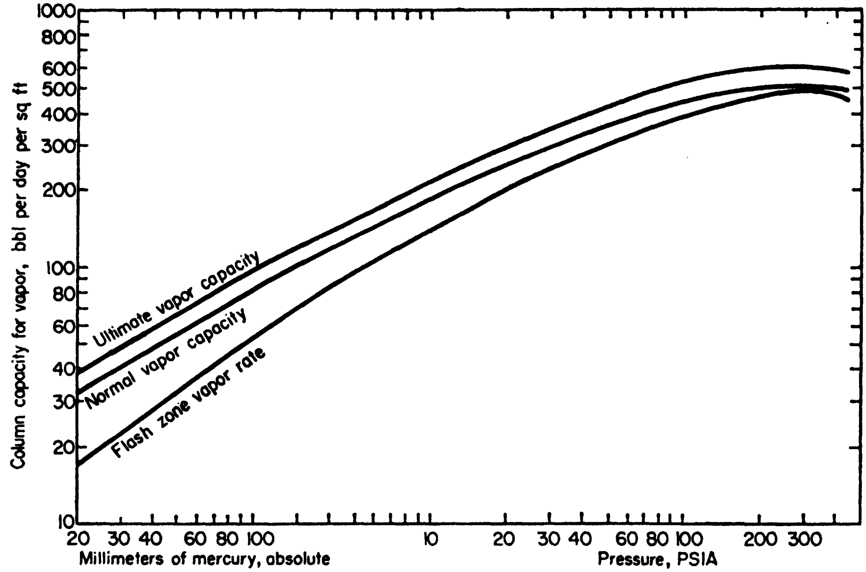

FIG. 3-15. Approximate vapor capacities of bubble-cap columns (2).

Thorough treatments of tray design and column sizing have been published by Davies (15) and Bolles (6). To simplify the design problem, Munk (52) recommends that designs be limited to a number of standardized patterns, for which design charts can be prepared for general use. Munk presents nine such charts, on which areas of satisfactory performance are indicated on plots of vapor rate per bubble cap against liquid rate per inch of weir. For rough calculations, column diameter can be estimated from vapor flow rates and tower pressures, as shown (2) in Fig. 3-15, and tray spacing may be assumed to be 2 ft. Because of entrainment problems, a lower vapor capacity may be used at feed inlets, as indicated.

If a column is to operate over a wide range of flow rates, flexibility is important. In such cases, the minimum permissible flow rates must be determined as well as the maximum; it is then often convenient to establish the whole range of conditions of satisfactory operation, as illustrated by the unshaded area in Fig. 3-16. Below the unshaded area, vapor rate is too low to maintain steady flow through the caps, and pulsations occur. In the lower range of satisfactory vapor loads, liquid loading is limited by hydraulic gradient; too high a flow rate causes an excessive liquid gradient on the tray, which results in uneven distribution of vapor to the bubble caps. In the higher range of satisfactory vapor loads, liquid loads are limited by high pressure drop and consequent flooding. Vapor load is limited by slot loading at low liquid loads and by entrainment at high liquid loads.

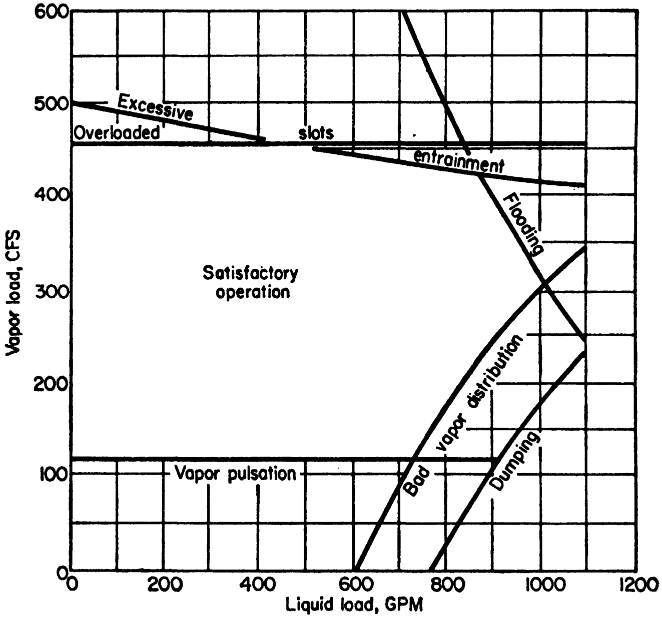

FIG. 3-16. Performance of a typical tray.

If an existing column is poorly designed or is to be used for a new operation, minor changes often improve operations considerably (71).

Sizing of Packed Columns. Packing requirements for packed columns are usually estimated from the theoretical plates required and the "height equivalent to a theoretical plate," or HETP. Unfortunately, HETP's vary with tower diameter, and there are few published data on hydrocarbon distillations in large units. Some data are given by Coulter (14), who mentions the following rules of thumb for design:

1. The diameter of the column should be at least eight times the diameter of the packing.
2. Columns with diameters greater than 18 in. give erratic results, at least with packings like Raschig rings.
3. The liquid-handling capacity goes down as the viscosity of the reflux liquid goes up.

A generalized correlation of the liquid-handling capacities of packed columns has been published (44).

Hydraulic Gradient. To provide the driving force for liquid flow, the liquid level must be higher on the inlet side of a crossflow tray. Thus, the resistance to vapor flow will be greater there, and more vapor will pass through the outlet side unless something is done to prevent it. Some crossflow of vapors results, countercurrent to the flow of liquid, and the crossflow can seriously reduce the capacity of large-diameter columns, especially if the girders supporting the trays are transverse to the crossflow (34). Probably the simplest way to compensate for hydraulic gradient in a bubble-cap tower is to raise the bubble caps at the inlet end (47). To achieve the same result with a sieve tray, fewer (or smaller) perforations may be used at the outlet end than at the inlet. Hydraulic gradient is of particular importance in vacuum units because of their large diameters and the low liquid levels usually employed on the trays to minimize pressure drop (47).

Other Considerations. Minor design problems include the design of liquid draw-offs and reboiler piping and the specification of manways. In designing liquid draw-offs, care must be taken to ensure that reasonable fluctuations in operation will not unseal the downcomers to the draw-off trays. This point is important when a large fraction of the downflowing liquid is withdrawn. Unsealing of a draw-off can result in flooding of the column.

Most reboilers are of the thermosiphon type,* and thus their operation could be limited by the piping between the column and reboiler. The capacity of the connecting piping should therefore be carefully considered.

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* A thermosiphon reboiler is located below the points from which the liquid to be reboiled is withdrawn from the column and to which mixed liquid and vapor is returned. The static head of the liquid in the piping to the reboiler is greater than the static head of the mixture in the piping returning to the column. This difference provides the head for flow.

Manways are usually included in fractionating columns to provide access for maintenance work. For vacuum units, manways are recommended at each tray to facilitate the removal of coke (5). For other columns, manways are used less frequently, and access to the intermediate trays is provided by making a section of each tray conveniently removable. Bolles (6) suggests 20 trays as the maximum number between manways in large-diameter columns, 10 in small-diameter columns. He also recommends that manways be 20 in. in diameter.

Control of Operations

Most petroleum fractionators are controlled by automatic instruments. Controlling product quality is the aim, but control is usually achieved indirectly by controlling operating conditions, such as temperature at some point in the column, column pressure, and reflux, feed, or product rates. The particular setup used will depend upon the particular application, and there are a large number of possible arrangements (68). Whatever the system, the controls should be designed to compensate gradually for any change in operations. Because there is a lag between the changing of a control instrument and attaining the new steady state, abrupt changes of the control instruments would cause a column to cycle.

The actual operation of a distillation unit may "wander" from the optimum because of, for example, changes in feed quality or of instrument calibration. On the other hand, there will always be some fluctuations in the operation, and it is sometimes difficult to differentiate a real change in operations from a normal fluctuation. This problem can be resolved by the application of statistics (17).

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CHAPTER 4

OTHER SEPARATION PROCESSES

Although distillation is usually the preferred separation technique, other processes are sometimes better. Indeed, some separations cannot be effected by distillation, and, for these, other techniques must be used. Prominent among the other processes are absorption, stripping, and extraction. Adsorption and crystallization are also used commercially, and thermal diffusion, rotary distillation, molecular distillation, gas chromatography, clathration, and permeation are of interest.

ABSORPTION AND STRIPPING

In modern refining only a small share of the virgin fractions from crude distillation is suitable for blending directly into final products. The bulk of the virgin materials must be processed to rearrange their molecular structures or to "crack" them down into smaller molecules. Even though catalysts are often used in these operations to direct the reactions along desired lines, side reactions occur which produce unwanted gases, and the products are usually mixtures of gaseous and liquid hydrocarbons. The uncondensed gases include some vapors of normally liquid hydrocarbons,* and the condensate contains some dissolved gases. To recover the condensable vapors from the "wet" gases, absorption is usually employed. Stripping is used to remove dissolved gases from the liquid product.

Principles of Absorption

If a gaseous hydrocarbon is thoroughly mixed with a liquid hydrocarbon, the gas dissolves in the liquid until the vapor pressure of the solution reaches the pressure of the system. If a mixture of vapors is used, each component goes into solution, the components with the lower vapor pressures having the greater tendencies to dissolve. By use of this principle, heavier components can be separated from a gaseous mixture and concentrated as an "absorbate" dissolved in a "lean oil." Subse-

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* The uncondensable gases are saturated with the vapors of heavier hydrocarbons in the same sense that air may be saturated with water.

quently, the absorbate is separated from the lean oil by distillation or by stripping.

Operating Variables. Absorption is increased by an increased usage of lean oil. It is also favored by increased pressures and by reduced temperatures. If the pressure is raised, more absorbate is dissolved in raising the vapor pressure of the solution to the pressure of the system.

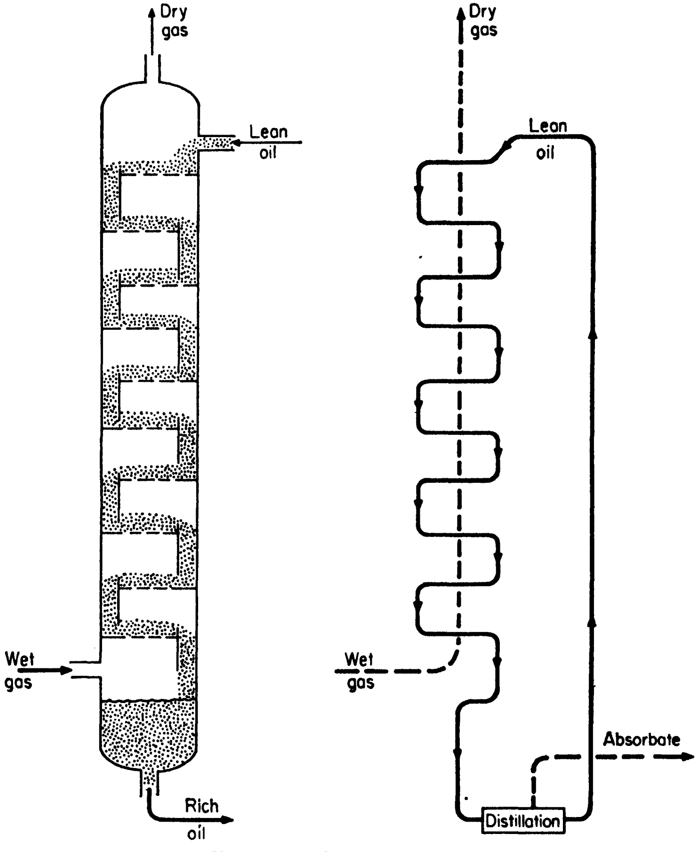

FIG. 4-1. Absorption tower.

Also, more absorbate is needed if the temperature is lowered, because the vapor pressures of the absorbed materials are lowered.

Staging. As in distillation, staging improves separation; it increases the recovery of heavier components in the absorbate and the rejection of lighter components to the "off gas." As illustrated in Fig. 4-1, countercurrent contacting columns are used in absorption, just as they are in distillation. The reason may be seen by comparing the two processes. In both of them, vapors pass up a column countercurrent to a downflowing liquid—lean oil plus absorbate in absorption, reflux in distillation. Absorbate performs the same function as does reflux in a distillation column. (The function of the lean oil is merely to permit the absorbate to condense at a lower pressure or at a higher temperature than it otherwise would.) Thus, increasing the number of stages "sharpens" the separation in absorption, just as it does in distillation.

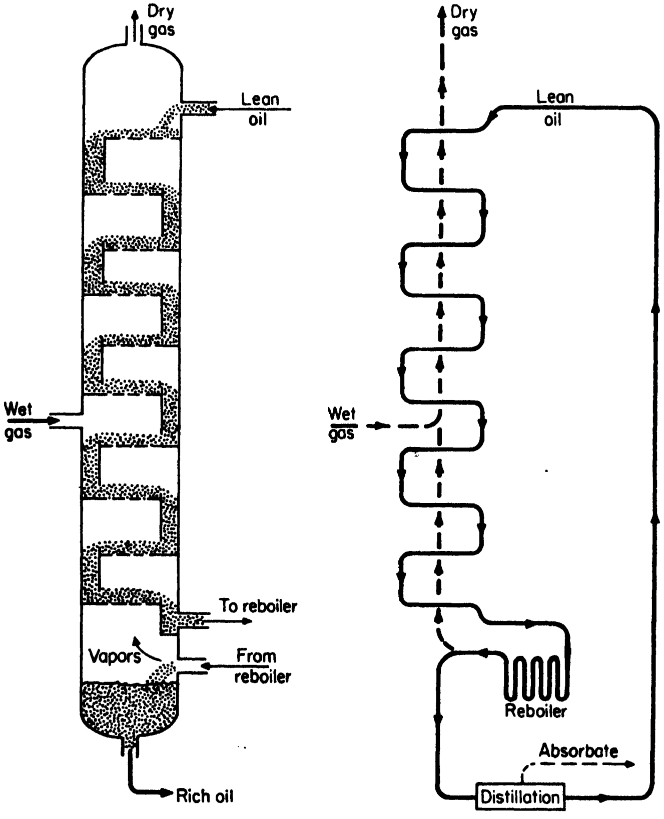

FIG. 4-2. Reboiled absorber.

The above comparison suggests that a refrigerated distillation unit should be able to do the same job as an absorption unit does. As a matter of fact, it can—and does. Refrigerated distillation competes with absorption in the recovery of ethylene from lighter gases.

Reboiled Absorbers. Inasmuch as a simple absorber has no trays below the feed inlet, it corresponds to a rectifying distillation column. Sometimes the absorbate contains sufficient light gases to interfere with subsequent processing. To eliminate these light gases, a stripping section may be added at the bottom of the absorber, as illustrated in Fig. 4-2. From a functional standpoint, the purpose of a stripping section is exactly the same as in a distillation column, i.e., to increase the purity of the heavy product. Because some of the desired products are stripped out with the light gases, more lean oil is required when a stripping section is used.

Lean Oils. Lean oils are usually high-boiling gasoline fractions or distillate-fuel stocks like kerosene. Whenever a choice is possible, factors that should be considered include absorption capacity, lean-oil loss, viscosity, and stability.

The absorption capacity of a lean oil depends upon its molecular weight and its composition. Because absorption capacities of liquids are molal functions, lighter oils, which have lower molecular weights, have higher absorption capacities on a weight basis. Because any hydrocarbon oil has a greater capacity to absorb chemically similar materials and because most of the vapors to be absorbed are paraffinic, paraffinic lean oils are preferable. The molecular weights of lean oils can be estimated from their physical inspections (28).

In so far as the lean oil is concerned, an absorber functions as a stripper, and a small amount of the lean oil is carried off as vapor in the off gas. The lower the molecular weight of the lean oil, the greater is the lean-oil loss. This disability must be balanced against the greater absorption capacity of the lower-molecular-weight oil.

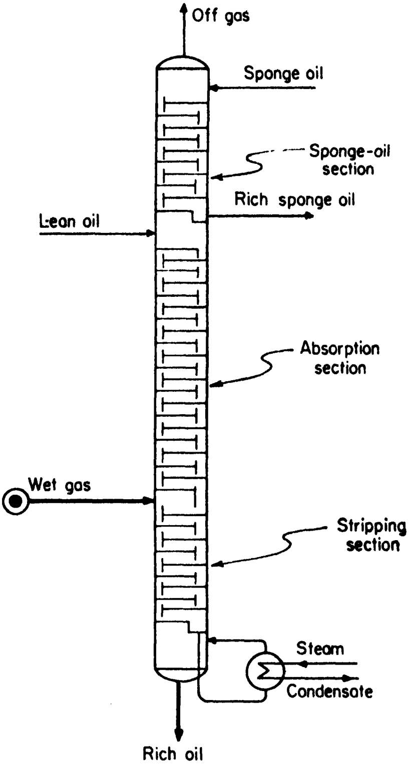

FIG. 4-3. Reboiled absorber with a sponge-oil section.

The rate of mass transfer in absorption depends principally on the viscosity of the lean oil (18,46). Because higher rates of transfer are obtained with less viscous, lower-molecular-weight oils, their use minimizes the tray or packing requirements for a given operation.

Chemical stability is important when the lean oil is intended to be retained in the system for a long time—when its replacement rate is low. When the lean oil is a product of the operation and mixes with the circulating oil, the replacement rate is high, and stability is of secondary importance.

Sponge Oil. The capacity advantage of a low-boiling lean oil can be obtained without the disadvantage of high lean-oil losses. This desirable objective is achieved by passing the off gas through another absorber (or absorber section) countercurrent to a high-boiling "sponge oil," which absorbs the vaporized lean oil. A column incorporating a sponge-oil section, and a stripping section as well, is shown in Fig. 4-3.

Principles of Stripping

Stripping is the reverse of absorption. In stripping, a gas, at a temperature well above its dew point, is passed through a column countercurrent to a downflowing liquid. Liquid vaporizes into the gas stream until the gas stream is saturated. If the liquid is a mixture of hydrocarbons, its lighter components have greater tendencies to vaporize. Thus, lighter hydrocarbons can be stripped away from heavier ones. Stripping is favored by raising the temperature, lowering the pressure, or increasing the usage of stripping gas. As in the cases of distillation and absorption, the sharpness of the separation is improved by staging the operation by the use of plates or packing in a countercurrent column. The downflowing liquid and the stripped vapors perform the same functions as in distillation; the stripping gas merely permits the lighter components to vaporize at a higher pressure (or at a lower temperature) than would otherwise be possible.

Sometimes, a simple stripper would vaporize excessive amounts of the heavier components. In such cases a refluxed rectifying section may be provided above the feed to "knock back" the heavier hydrocarbons.

Equipment

Inasmuch as absorption and stripping columns perform the same function as do distillation columns—the contacting of an upflowing gas with a downflowing liquid—the same kinds of equipment are used for all three processes. The liquid flow rates (relative to the vapor rates) are often higher for absorption and stripping than for distillation; therefore, a greater liquid-handling capacity may be required. With the provision of more liquid-handling capacity, any of the various trays and packings used in distillation may be used. In addition, a "recycling tray" is sometimes used in absorption, and high efficiencies are claimed for it (56). A recycling tray is a sieve tray modified by the addition of boxlike baffles that blank off 40 to 60 per cent of the perforations. The baffles divide the tray into a series of alternating gas-contacting and liquid-coalescing sections, so arranged that a portion of the liquid from each coalescing zone is recycled back to the preceding gas-contacting zone. Kascade trays are also claimed to have high capacities (12).

Operations

In petroleum-refining operations, an absorption unit generally includes distillation facilities to recover the absorbate. As illustrated in Fig. 4-4, the simplest absorption unit consists of an absorption column and a distillation column in which the absorbate is separated from the lean oil.

Many modern absorption columns are reboiled. The use of a reboiled absorber permits the concurrent stabilization* of the liquid usually produced in conjunction with wet gas. How this may be done is illustrated in Fig. 4-5. Wet gas and "raw" gasoline from a catalytic-cracking unit are charged together to an intermediate point in a reboiled absorber, and "condensables" are absorbed from the wet gas in the upper part of the column. Rich oil (lean oil plus absorbate) passes into the stripping section together with the raw-liquid feed. There, dissolved gases are stripped out, to pass back into the absorption section. Bottoms from the reboiled absorber are charged to a distillation tower, where light gasoline is separated from heavy gasoline. Part of the heavy gasoline is cooled and returned to the absorber as lean oil. To avoid losses of gasoline vapors in the off gas, a sponge-oil section is provided at the top

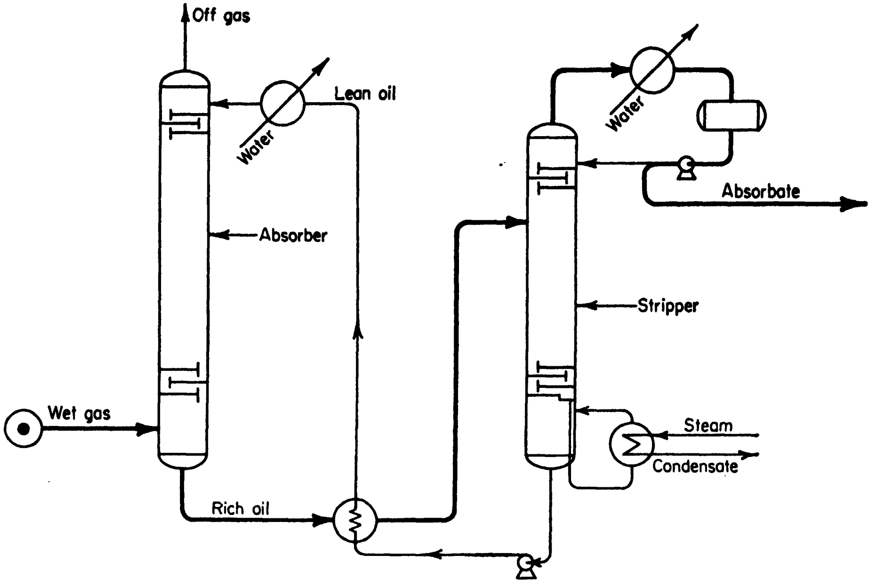

FIG. 4-4. Simple absorption unit.

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* "Stabilization" consists of removing dissolved gases from liquid hydrocarbons. As applied to gasolines, the term may mean depropanization, or it may mean removing some butanes as well—enough butanes for the gasoline to meet a vapor-pressure specification.

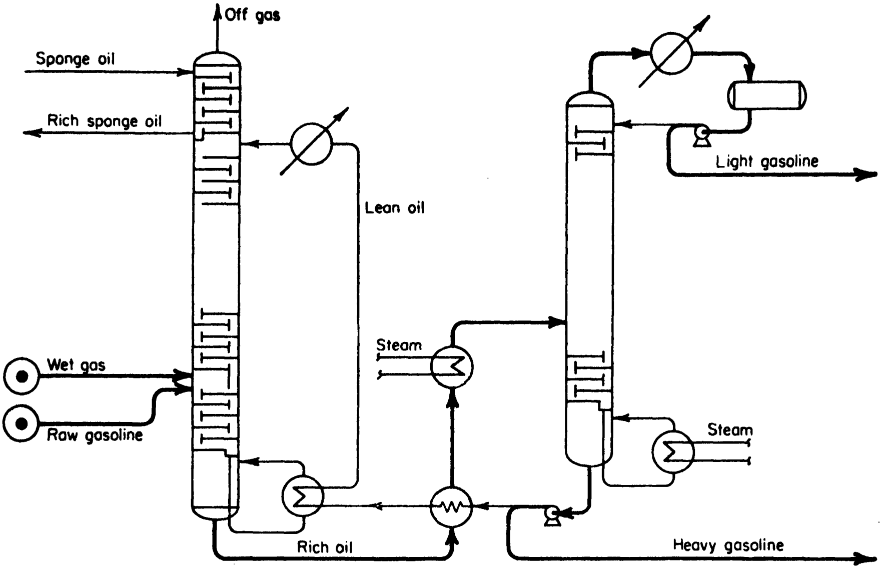

FIG. 4-5. Reboiled absorption unit.

of the absorber. Heavy "cycle oil" from a catalytic cracker is used as sponge oil, and the rich sponge oil is returned to the catalytic-cracking unit, where the absorbed gasoline is recovered in the primary fractionator.

Design of Absorption and Stripping Equipment

Design of absorption and stripping columns parallels the design of distillation columns. First, the degree of separation is specified in terms of how components split between final products. Second, the operating pressure and temperature are chosen, and tray and lean-oil (or strippant) requirements are determined from fundamental considerations. Finally, the equipment is sized on the basis of empirical correlations. Frequently, a portion of absorbed gas is recycled from a subsequent stripping operation, and this complicates the calculations somewhat.

Separation Criteria. Absorptions are usually specified in terms of the recovery of a particular component of the wet gas, for example, butanes. In a simple absorption column, the specification of one recovery and of the number of trays sets the recovery of each of the other components (71). In reboiled absorbers, the maximum retention of one of the lighter components must also be set to define the separation.

Strippers are specified in terms of how much of a specific light component is eliminated from the liquid. If a rectifying section is not provided, setting the stripping of one component and the number of trays also sets the elimination of all other light components. For refluxed strippers, the minimum retention of some heavier component must also be set to define the separation.

Pressure. Because increasing pressure reduces lean-oil requirements in absorption, the relative costs of compressing wet gas and circulating lean oil must be weighed. When gas is available at elevated pressures, say 100 psi or higher, further compression is seldom used. When the gas is produced near atmospheric pressure, on the other hand, it is usually compressed to a higher pressure. A compression ratio of four or five to one is frequently employed.

Stripping is favored by reduced pressure. If condensation of the stripped vapors is not a consideration, the operating pressure is the lowest at which the overhead vapors can be conveniently handled. If condensation of the overhead vapors is desired, the operating pressure is the lowest at which they can conveniently be condensed.

Temperature. Because absorption is favored by lower temperatures, absorption temperatures are the lowest that can be readily attained. With 80°F cooling water, for example, 100°F is a reasonable lean-oil temperature.

Stripping is favored by higher temperatures; therefore, the costs of raising the temperature must be balanced against the costs of using stripping gas. If steam is used for stripping, the temperature must be higher than its condensing temperature at the tower pressure, or it will condense.

Because vapors are condensed in an absorber and liquids vaporized in a stripper, there is a temperature gradient across each tower. In a simple absorber, the bottoms temperature is higher; in a simple stripper, the reverse is true. The gradient is usually less than 40°F. (With reboiled absorbers or refluxed strippers the gradient is, of course, much greater.) Sometimes the temperature rise across an absorber is high enough to warrant withdrawing the lean oil from some intermediate point in the column, cooling it in a heat exchanger, and returning it to the column. Such "intercoolers" are not often used in petroleum refining.

Trays, Lean Oil, Stripping Gas. Setting the operating pressure and lean-oil temperature in an absorber sets the equilibrium vapor-liquid relationships for each of the components. Other factors important to the separation are the number of trays provided and the amount of lean oil used. If the lean oil is recirculated, the degree of lean-oil stripping is also a factor, but usually a secondary one because stripping is substantially complete in most cases. To some extent, trays and lean-oil rates are interchangeable.

Precise separation calculations (66) can be made by assuming a lean-oil rate and calculating stepwise from one theoretical plate to the next by means of heat and material balances and equilibrium relationships (75). Such calculations are tedious, and simpler, less exact methods have been devised that are adequate for most engineering work (22,65). The same approach applies to strippers except that stripping gas (rather than lean oil) is the variable quantity.

Usually, 20 to 30 actual trays are provided for absorption, 10 or more for stripping (37). Inasmuch as tray efficiencies in absorption are usually in the range of 20 to 30 per cent (27,49), 20 to 30 actual trays constitute 4 to 9 theoretical trays. It has been shown that tray efficiencies for different components vary. However, inaccuracies in tray efficiencies are important only for the components whose absorption or stripping factors* are close to unity. In absorption, lighter components rapidly approach the absorption that would be obtained with an infinite number of trays, and heavier components are almost completely absorbed (49); in stripping, the reverse is true. Empirical correlations for efficiency have been published (18,46).

Recycle Calculations. An absorber is usually part of a vapor-recovery system, which includes stripping equipment. Frequently it is not convenient to condense all the absorbate taken overhead in the stripping column, and the uncondensed portion is recycled. Recycling complicates design calculations, because determining the composition of the recycle stream is a trial-and-error proposition. A procedure for minimizing the number of trials has been published (71).

Sizing. The formulas for sizing absorbers and strippers are the same as for fractionators except that a greater safety factor compensates for greater foaming tendencies. Typically, a factor of 1.3 is applied to the cross-sectional area calculated on the basis of distillation-column correlations.

EXTRACTION

Solvent extraction is one of the oldest processes used in the refining of petroleum, the first application having been made in 1911. Originally, upgrading of kerosene was the major use, but the improvement of lubricating oils is now much more important. More recent applications, which will probably expand, include the upgrading of charge stocks to catalytic cracking and the separation of light aromatics from gasolines.

Principles of Extraction

Extraction is possible because different liquids have different affinities for each other. Some are completely miscible in all proportions; others

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* Absorption factor $= \dfrac{L}{KV}$ Stripping factor $= \dfrac{KV}{L}$

where L = moles of downflowing liquid
V = moles of rising gas
K = vapor-liquid equilibrium ratio for a component at conditions of operation

are almost immiscible. When the components of a solution exhibit such differences, it can be separated into two fractions, usually of different chemical species, by contacting the feed stock with a suitable liquid. As in other separation processes, a single contacting stage does not normally suffice, and countercurrent multistage units are required. Also "refluxing" may be necessary if a pure product is desired.

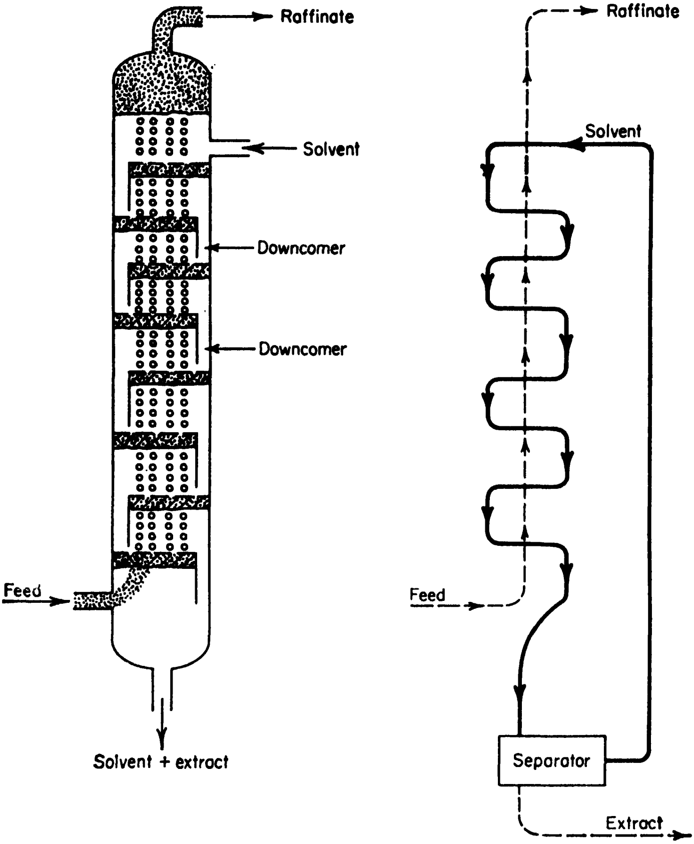

FIG. 4-6. Simple extraction unit.

Terms. Terms used in extraction include "solvent" for the extracting agent, "solute" for the readily soluble material in the feed, "extract" for the material removed from the feed, "raffinate" for the nondissolved product, and "reflux" for extract returned to the extractor. "Lean solvent" refers to the solvent as charged to the extractor; "rich solvent" to the solvent-extract solution leaving the extractor.

Staging. Various methods may be used for contacting the feed and solvent. Figure 4-6 shows a typical operation, in which a sieve-tray column is used and where the solvent is denser than the feed. Lean solvent enters above the top plate, passes across it, flows by gravity through a downcomer to the next plate, across that plate to the next downcomer, and so on to the bottom of the column. Feed enters below the bottom tray and passes up through the perforations in each tray until it finally passes out the top of the column as raffinate. As it rises, the feed contacts progressively leaner solvent on each tray, and thus on each tray it loses material to the solvent.

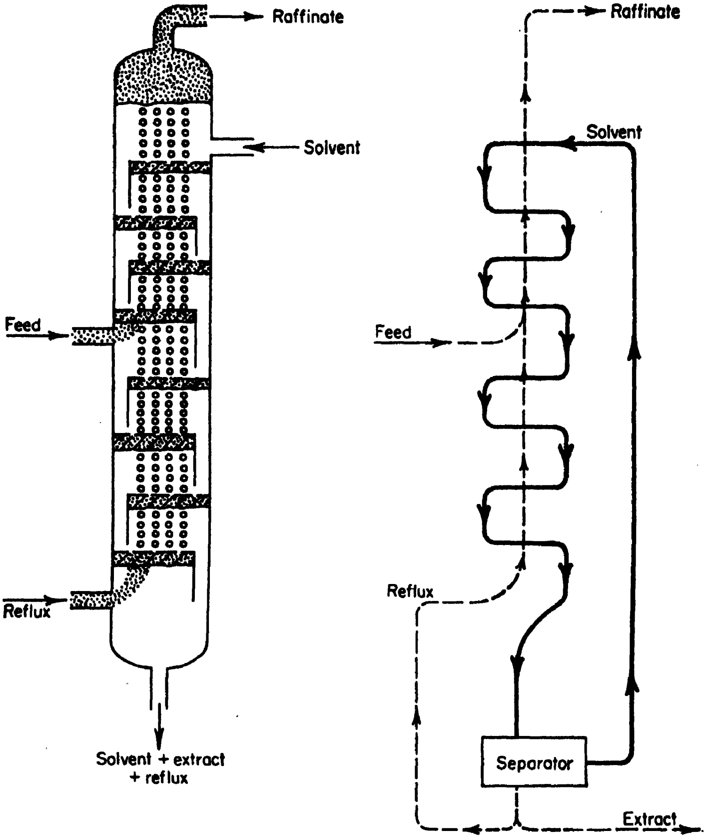

FIG. 4-7. Extraction with reflux.

The advantages of staging can be seen qualitatively by considering what happens at the lowest contacting stage as the number of stages is increased. With only one stage, the rich solvent is in equilibrium with the raffinate, which contains much less solute and much more diluent than the feed did. As the number of stages is increased, the material rising from the bottom stage approaches the composition of the feed;

consequently, the concentration of the solute in the solvent from that stage increases, and the concentration of the diluent decreases. With an infinite number of stages, the rich solvent would be in equilibrium with the feed.

Reflux. Frequently, a simple extraction system will not give a pure enough extract, and reflux must be used, as illustrated in Fig. 4-7. In this system, several stages are provided below the feed and a portion of the extract is returned to the base of the column. Rising up the column, the reflux displaces diluent from the solvent, and thus increases the purity of the final extract. Because the capacities of most solvents go down with temperature, reflux can be induced by operating the solvent-outlet end colder than the solvent inlet or by cooling the rich solvent taken from the tower and returning the liquid which separates. The use of reflux increases the solvent-circulation requirements.

Use of Wash Oils. With some solvents, there is a maximum solute concentration that cannot be exceeded. When sulfur dioxide is used to extract light aromatics, for example, the maximum solute concentration of aromatics in the extract is about 75 per cent; above that concentration the hydrocarbon stream is completely miscible with the solvent. Even with sulfur dioxide, however, high-purity aromatics can be obtained by washing the extract with a paraffinic oil of a different boiling range. Wash oil displaces diluent in the extract. Subsequently, the wash oil is separated from the extract and recycled.

Solvents. The first requirement for a solvent is that it be selective—that it have a reasonable capacity to dissolve one or more components of the feed and only a small capacity for the others. Second, its density must be different from that of the raffinate so that the rich solvent can separate from it. Also, the solvent must be readily separable from the extract; distillation is the usual separating technique. Other desirable features are low cost, chemical stability, and a simple means of separating traces of solvent from the product streams.

Because the mutual solubilities of liquids change with temperature, the use of a given solvent for a given application is restricted to a narrow temperature range. Generally, higher temperatures increase the dissolving capacity of a solvent but lower its selectivity for one hydrocarbon over another. By way of example, for the extraction of gasoline-range aromatics with sulfur dioxide, low temperatures are required for reasonable selectivity, say −20°F. On the other hand, hydrocarbons in the lubricating-oil range are less soluble in sulfur dioxide, and temperatures of 50 to 75°F must be used to obtain satisfactory dissolving capacities.

Many solvents are miscible with water, and their solvency powers can be modified by dilution. Increasing the water content improves the selectivity of such a solvent, but reduces its capacity.

Extraction Equipment

In the design of extractors the principle problem is to provide sufficient dispersal of one of the phases into the other, so that material may transfer between them. A wide variety of designs have been used, and an even wider variety have been proposed (45). In the petroleum industry, the most popular types have been mixer-settler combinations, packed columns, perforated-tray columns, and baffle columns. A "rotating-disc contactor" was commercialized about 1955, and "pulsed" columns and centrifugal extractors have been proposed.

Mixer-Settlers. Mixer-settlers have been used for the extraction of lubricating oils to improve quality (45), for separation of butadiene from a butanes-butenes-butadiene mixture (45), and for extraction of mercaptans from gasoline (60). Usually four to eight countercurrent stages are employed, although as many as fourteen have been used (60). As shown in Fig. 4-8, each stage consists of a mixing chamber, a settling chamber, and a pump. For the mixing chamber, a cylindrical tank with vertical baffles at the walls is usually used. If reflux is not employed, the feed is charged at one end of the chain of stages, solvent at the other. If reflux is used, solvent and reflux are charged to opposite ends, feed to an intermediate stage. An objection to mixer-settlers is the many pieces of equipment required. Various designs have been proposed (9,14) to house the equipment in one shell and thus reduce its complexity. Although some of these designs have been used commercially (26), no petroleum-refining applications have been reported.

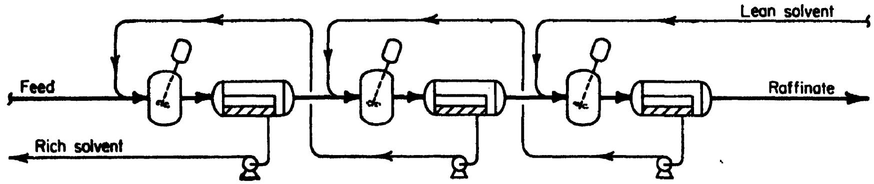

FIG. 4-8. Three-stage mixer-settler extractor.

Packed Columns. Open, "wetted-wall" columns could be used for extraction, but the contacting efficiency would be poor because the contact surface for interchange of materials would consist only of the area of the cylindrical shell. If a packing is added to such a column, one of the countercurrent liquids spreads out over its surface and thereby increases the contacting area. The packing also increases turbulence, and both factors improve the transfer of materials. Packed columns have been used (45) for the extraction of aromatics from lubricating oils and from kerosene, and of hydrogen sulfide from liquid propane. One-inch Raschig rings are popular. A packed height of 20 to 50 ft is typical, although packed heights of 100 ft have been employed (61). In large-diameter columns, liquid redistributors are used at intervals of four to ten feet. Typical commercial columns provide 1.4 to 4 theoretical stages (26).

In packed columns, it is usually desirable to hold the interface between the raffinate and solvent phases near the bottom, because the packing is preferentially wetted by the solvent. Sulfur dioxide is an exception (at least with heavy feeds) because its low viscosity promotes transfer of material between phases (26).

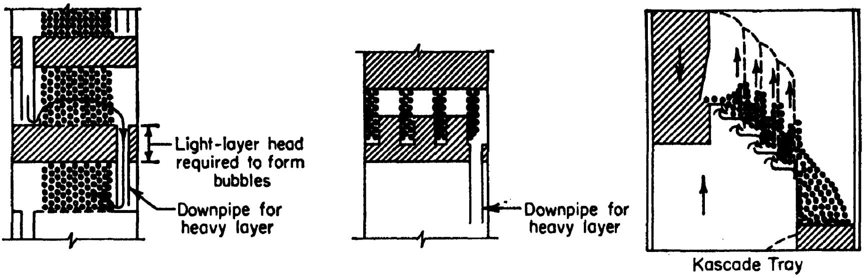

FIG. 4-9. Perforated-tray columns (45).

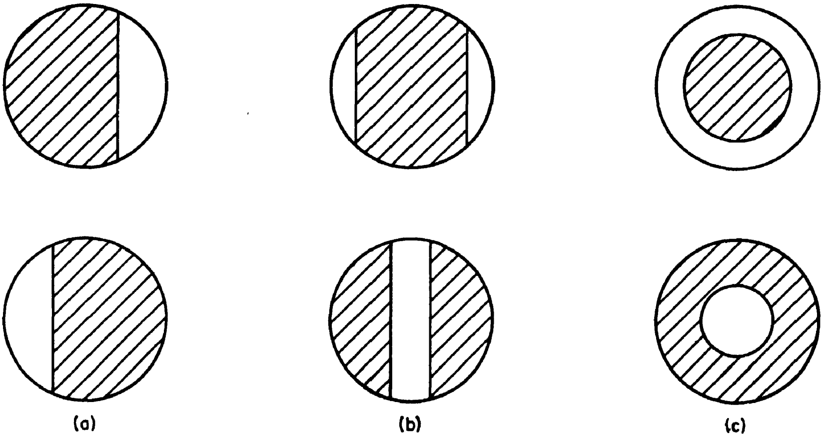

FIG. 4-10. Baffles used in solvent-extraction columns. (*a*) Side-to-side. (*b*) Center-to-side. (*c*) Disc and doughnut.

Perforated-tray Columns. Perforated-tray columns appear to have been the most popular extractors, particularly for lubricating oils (45). Fifteen to twenty trays are used commonly. Three types of perforated trays are shown in Fig. 4-9. The corrugated tray with perforations in the vertical walls is used where difficulties with solids are anticipated. The Kascade tray may be considered a special type of perforated tray (45).

Baffle Columns. In some columns, simple horizontal baffles are used to force the countercurrent liquids to zigzag. Three types are used: "side-to-side," "center-to-side," and "disc-and-doughnut"; these are illustrated in Fig. 4-10. For each such baffle, the contacting efficiency is low, but a reasonable column efficiency is obtained by spacing the baffles only 4 to 6 in. apart. Because the cost of dismantling is high, this type of column is not recommended where precipitates may form that are removable only by mechanical means (45).

Rotating-disc Contactors. Because packed, perforated-tray, and baffle columns rely on gravity alone to provide the impetus for mixing, their liquid-contacting efficiencies are low. To augment the force of gravity, rotating-disc contactors (60) employ mechanical power. The internals of a rotating-disc contactor are similar to disc-and-doughnut baffles, except that they do not overlap. Also the discs are attached to a rotating central shaft, as shown in Fig. 4-11, and their rotation disperses one of the counterflowing liquids into the other. Preferably, the incoming liquid streams are brought into the system tangentially in the direction of rotation. Because they are high-efficiency devices, rotating-disc contactors are favored by conditions which require a considerable number of stages. When seven stages are required, the cost of a rotating-disc contactor is claimed to be less than half that of a mixer-settler system or a packed column (60,61).

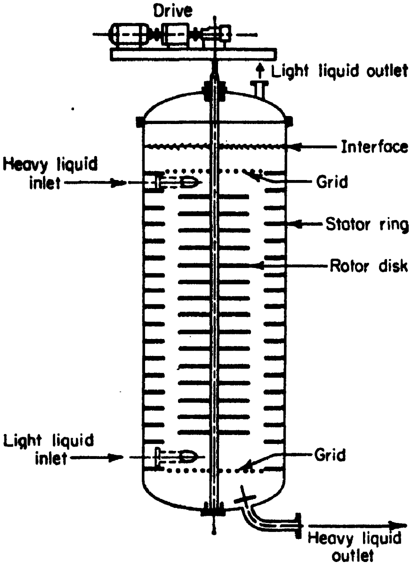

Fig. 4-11. Rotating-disc contactor (60).

Other systems employing compartmented mixers have been proposed (48,63), but no petroleum applications have been reported.

Pulsed Columns. Improved contacting can also be obtained by "pulsing" a column, i.e., by rapidly withdrawing liquid and returning it to the same point cyclically. Either sieve-tray columns or packed columns may be pulsed (13,62). With sieve trays, no downcomers are used, and the holes are so small that no liquid would flow if the columns were not pulsed (69). On the upstroke, the lighter liquid is forced upward through the holes. On the downstroke, the heavier liquid is forced downward. Typically, the liquids are pulsed 60 times per min at an amplitude of 0.5 to 0.9 in. High contacting efficiencies are obtained, but at the cost of low throughputs, increased tendencies to emulsify, and pulsation costs. Pulsed columns were developed for extracting atomic wastes, and no commercial petroleum-refining applications have been reported.

Centrifugal Extractors. Centrifugal force is also used to improve contacting efficiency. A centrifugal contactor consists (1,3,16) of a spinning rotor containing a perforated spiral chamber through which two liquids pass countercurrently. Its principal uses have been in the manufacture of pharmaceuticals, where its low holdup is particularly advantageous.

Extraction Operations

In most petroleum applications, solvent extraction removes materials of low hydrogen content—principally aromatics—from materials of higher hydrogen content. Extraction was first used to upgrade kerosene by removing aromatics, which burn with a smoky flame. Next it was used to upgrade lubricating oils by removing aromatic materials with low viscosity indexes, and this is the most important present application. Extraction is also used today to improve charge stocks to catalytic cracking, to improve the qualities of light catalytic cycle oils as heating oils, to recover light aromatics from gasoline stocks, to separate *i*-butene from butane-butene streams, and to remove mercaptans from gasoline.

The extraction equipment proper is only a minor part of a commercial plant. Other facilities include a fractionation column for recovering extract from the rich solvent, and facilities for recovering, from the extract and raffinate, traces of solvent, which is usually too expensive to permit appreciable losses. The method used for recovering the solvent varies from system to system. By way of example, evaporation under vacuum is used to recover sulfur dioxide, steam stripping to recover phenol, and water washing to recover glycols, which are then fractionated from the wash water.

Prior to 1930, sulfur dioxide was the only solvent used commercially; solvent-recovery techniques were not sufficiently advanced to permit the use of other, more expensive materials (26). Today, various solvents are employed. Sulfur dioxide is used to extract petroleum stocks of all boiling ranges. Furfural is almost as versatile; it is used for extracting all petroleum stocks higher-boiling than gasoline. For the extraction of lubricating oils, phenol is also a popular solvent, and nitrobenzene, dichloroethyl ether (chlorex), and a propane–cresylic acids combination (Duo-Sol) are used to a lesser extent. Glycols are used to extract light aromatics from gasoline; and hydrogen fluoride has been proposed for removing coke formers and sulfur compounds from feeds to catalytic cracking and of sulfur compounds from kerosene. Sulfuric acid is used for the extraction of *i*-butene. For the preparation of residual crude oils as feeds to catalytic cracking, light paraffins may be used as extractants. Extraction of lubricating oils is discussed in Chap. 11, extraction of mercaptans in Chap. 14. The other operations are covered here.

Sulfur Dioxide. Although sulfur dioxide extraction (also called the Edeleanu process after its inventor) is applied to a wide variety of feed stocks, all the plants are similar, except for operating temperatures. Stocks in the gasoline range are extracted at about −20°F, lubricating-oil stocks at temperatures of 50 to 75°F, and intermediate stocks at intermediate temperatures. Typically, one volume of solvent is circulated per volume of charge stock. When a high-purity-aromatics product is desired, the process is modified by the addition of a wash-oil reflux step. When lubricating oils are processed, benzene may be added to the solvent to increase its capacity for dissolving heavier aromatics, but the addition lowers selectivity (26). For equal selectivities, lower temperatures are required when benzene is used.

A typical sulfur dioxide extraction plant is illustrated schematically in Fig. 4-12. After passing through a coalescer for the removal of free water, the feed is dried, cooled to extraction temperature by exchange with raffinate and with a refrigerant, and charged to the extraction column. Raffinate passes from the extractor to a set of three evaporators, in which sulfur dioxide is taken off. Rich extract from the bottom of the column passes to a second set of evaporators. The first evaporator in each set operates at 80 psi or higher—a pressure high enough that the vapors can be condensed without compression. Compression is required for the vapors from the other evaporators, the last of which operate at about 25 mm Hg absolute. (Two vacuum stages are used in order to reduce compression requirements, which would be high if all the sulfur dioxide were evaporated at 25 mm Hg.) Because water makes sulfur dioxide corrosive, a slip stream of the circulating solvent is distilled to reject it as bottoms, and thus hold the water content of the circulating sulfur dioxide below 0.05 per cent. Some sulfur dioxide is lost to the products, to the reject water, and in leakage. Typically, solvent losses may total about 0.15 lb per bbl of charge. A typical packed column for the extraction of light distillates contains about 30 ft of packing (26).

The plant of Fig. 4-12 is designed for the use of steam as a heating medium. If circulating hot gas-oil is used instead, higher temperatures are possible and the final vacuum evaporation stages can be omitted; with naphtha feeds, solvent recovery can be accomplished in one stage, and no compression is required (74).

Raffinates from sulfur dioxide extraction contain from about 1 to about 5 per cent aromatics, extracts from 55 to 80 per cent. In the recovery of light aromatics, higher concentrations are usually required. They are obtained by displacing the diluent materials with a wash oil such as kerosene, and then separating the wash oil from the product aromatics by distillation. Some wash oil passes into the raffinate, from which it is also separated by distillation.

Typical separations obtained by sulfur dioxide extraction are shown in Table 4-1; typical utilities requirements in Table 4-2. In operations that include the use of wash oil, 90 per cent benzene, nitration-grade toluene, and high-purity (99+ per cent) xylenes can be produced (74). Recoveries are: for benzene, 95 per cent; for toluene, 98 per cent; for xylene, 96 per cent (53). Benzene can be raised to nitration grade by azeotropic distillation with methanol at an over-all recovery of 90 per cent of the benzene in the charge to extraction (74). A detailed description of this type of plant has been published (57).

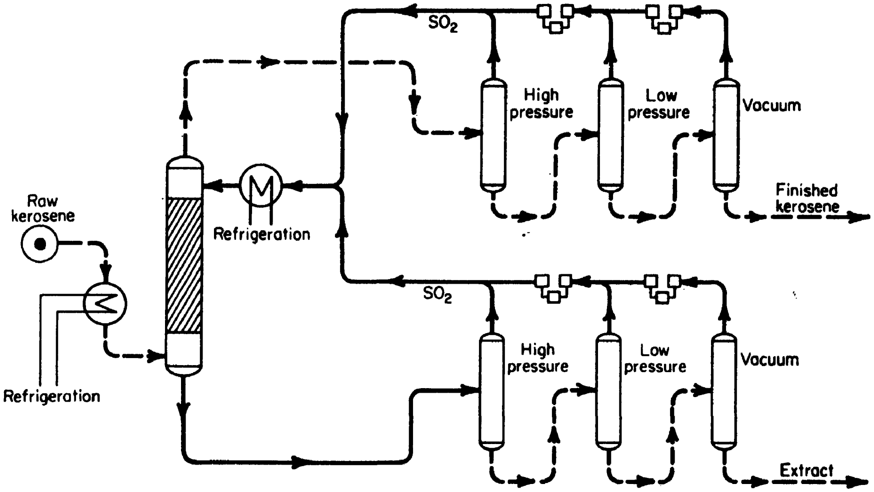

FIG. 4-12. Schematic diagram of SO_2 extraction plant.

Table 4-1. Separations Obtained by Sulfur Dioxide Extraction (15,74)

	Gas oil	Kerosenes		Diesel oil	Naphthas	
Extraction conditions:						
Solvent:feed, vol/vol	125	160	100	135	75	175
Wash oil:feed, vol/vol	0	0	0	0	0	75
Temperature, °F	30	8	0	21	−20	−20
Extract, vol %	23	23.5	15	25.0	20.6	53.4
Aromatics content, vol %:						
Feed	22.0	18.0	14	24.0	16.7	51.0
Extract	79.5	75.0	82	78.0	75.9	94.0
Raffinate	5.0	2.0	2	3.0	1.3	1.8

Table 4-2. Utilities Requirements of Sulfur Dioxide Extraction Plants (74)

	Gas oil	Kerosene	Naphtha	Naphtha
Extraction conditions:				
Solvent:feed, vol/vol	125	100	75	170
Wash oil:feed, vol/vol	0	0	0	75
Temperature, °F	30	14	0	−20
Utilities, per bbl of charge:				
Steam, lb	85	75	63	112
Power, kwhr	2.9	3.0	3.5	1.6
Water (85°F), gal	930	830	750	1,600
Fuel, M Btu	.....	.....	.....	329

In 1953 a price of $2,500,000 was quoted (53,74) for a plant to process 9,000 bbl per day of naphtha without wash oil, 10,000 bbl per day of kerosene, or 10,000 bbl per day of gas oil under the conditions of Table 4-2. The same price was quoted for a plant to process 4,000 bbl per day of naphtha with the use of wash oil and with benzene purification. Operating costs were quoted at 11 to 22 cents per barrel of charge.

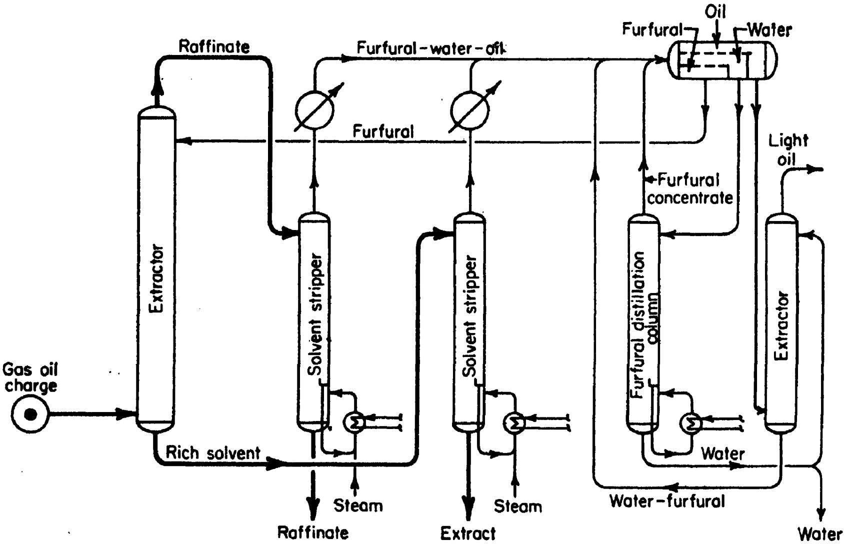

FIG. 4-13. Simplified furfural-extraction unit.

Furfural. The complexity of furfural extraction units depends upon the particular application. For the upgrading of diesel oils, heating oils, and charge stocks to cracking, a rough separation is usually adequate and a simple system may be used.* A typical design is shown in Fig. 4-13. Charge stock is introduced at the base of the extractor (when

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* A more elaborate system is required for lubricating oils, as discussed in Chap. 11.

reflux is not used) at a temperature in the range of 110 to 220°F; it rises countercurrent to the downflowing furfural which is brought into the top at a temperature between 200 and 290°F (26). Raffinate passes overhead to a reboiled stripper, where furfural is stripped out with the aid of steam. Furfural is also stripped from the rich solvent in a second, similar tower. The overhead vapors, which contain steam and some oil, are condensed and passed to a separator drum. Three phases separate. The heaviest phase is rich in furfural and is usually recycled directly to the extractor. The intermediate water phase is charged to a fractionator, from which enriched furfural is taken overhead and returned to the separator drum. The lightest, oil-rich phase is washed with water to recover furfural, and the wash water is also returned to the separator. By these operations, the overhead streams from the strippers are separated into recycle furfural, water discarded from the bottom of the fractionator, and a water-washed oil. Solvent losses are about 0.03% of the furfural circulated (26). Modern furfural units may utilize towers with about 20 feet of Raschig rings (or their equivalent), with redistributors at intervals of about four feet (26).

The circulating solvent in most furfural extraction plants contains about 5 per cent oil. A solvent fractionator is sometimes employed to eliminate this oil (10).

Typical furfural-extraction operations are given in Table 4-3 (10,53).

Table 4-3

Feed stock	Raffinate	Cetane no.		Sulfur, wt %	
	Yield, vol %	Feed	Raffinate	Feed	Raffinate
Light virgin gas oil	89.0	58.5	71.5	0.86	0.39
Light virgin gas oil	82.0	53.2	62.9	1.12	0.49
Light catalytic cycle oil	71.1	42.5	64.2	1.10	0.19
Light catalytic cycle oil	79.3	42.5	57.0	1.10	0.44
Light catalytic cycle oil	78.9	54.8	62.5	1.39	0.39

Glycol. Glycol–water (Udex) solutions are used for the extraction of light aromatics. When the products are used as petrochemical feeds, they must be pure; consequently a refluxed system is used. A schematic flow diagram is shown in Fig. 4-14. The feed stock (usually a catalytic reformate, although cracked naphthas may also be charged (6)) is fed to a refluxed extractor. Rich solvent from the extractor passes to a solvent stripper, from which extract is taken overhead with the aid of steam as a strippant, a portion of the extract being recycled to the extractor as reflux. Raffinate from the extractor is water-washed to recover dissolved glycol, the washings are combined with the solvent from the bottom of the solvent stripper, and the mixed stream is recycled to the extractor to complete the cycle. Typical Udex results when charging a catalytic reformate fraction (173 to 358°F) are given in Table 4-4 (53). The individual products shown in this table were fractionated from the Udex extract.

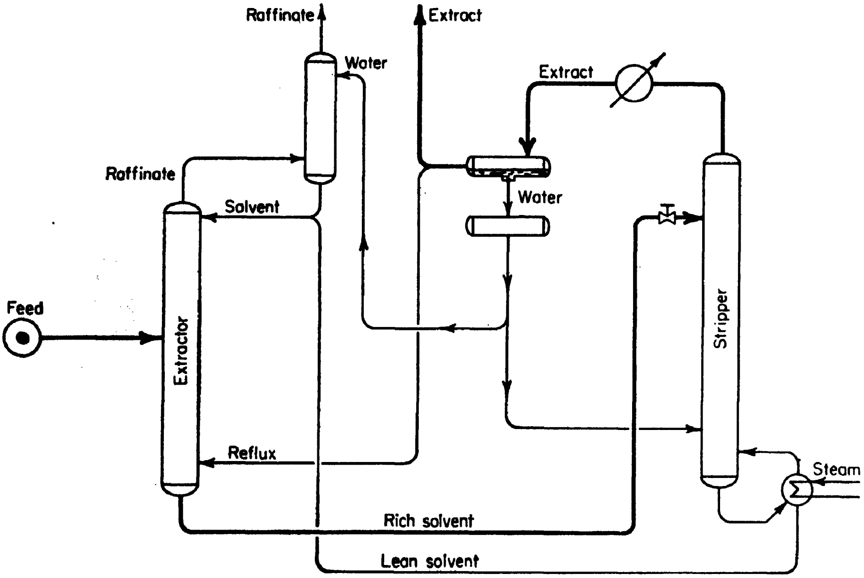

FIG. 4-14. Simplified Udex unit.

Table 4-4

Material	Per cent by volume		Per cent aromatics in fractionated product
	Of charge	Of extract	
Benzene	4.6	8.3	99.9
Toluene	24.0	43.0	99.8
Xylenes and ethylbenzene	20.8	37.2	99+
C_9 + aromatics	6.4	11.5	
Raffinate	44.2		

Hydrogen Fluoride. Except for the solvent, a hydrogen fluoride extraction unit is similar to a furfural unit. Extraction temperatures are low (100 to 125°F), as is the solvent circulation rate (0.15 to 0.3

volumes of solvent per volume of charge). Typical results are shown in Table 4-5 (53). Hydrogen fluoride is selective for the removal of sulfur compounds and condensed-ring aromatics (38,40). No commercial hydrogen fluoride extraction units have been reported.

Table 4-5

	Kerosene		Gas oil		Catalytic cycle oil	
	Charge	Raffinate	Charge	Raffinate	Charge	Raffinate
Solvent-to-oil ratio	0.30	.....	0.30	.....	0.17	
Yield, vol %	100	95	100	91	100	86
Sulfur, wt %	0.84	0.12	1.56	0.61	1.07	0.11
Gravity, °API	40.3	41.1	30.2	33.9	29.3	33.3

Light Paraffins. When reduced crudes are diluted with light paraffins, asphaltic materials are precipitated out and the metals content is reduced. When the object of the operation is to produce lubricating oils, the operation is called "deasphalting." When the object is to prepare charge stocks to catalytic cracking, the operation is called "solvent decarbonization." This process is discussed in Chap. 11.

Sulfuric Acid (i-butene). Isobutene is extracted from refinery butane-butene streams either to obtain pure *i*-butene or pure *n*-butenes, or both. Both materials are used for the manufacture of synthetic rubbers—*i*-butene for butyl and *n*-butenes for buna S. (Normal butenes are first converted into butadiene.) Isobutene is extracted into 65 per cent sulfuric acid, usually in a two-stage mixer-settler unit (4). The first stage may operate at about 100°F, the second at 65°F. (The higher temperature is used in the first stage to obtain a high extraction rate, the lower temperature in the second stage to obtain high selectivity.) Because selectivity in this system depends at least partly upon differences in extraction rates, contact times are rigidly controlled. Rich solvent is regenerated by dilution with water to 45 per cent acid, followed by stripping to remove the *i*-butene. The acid is then reconcentrated to 65 per cent and recycled. Typically, 85 per cent of the *i*-butene may be recovered in a concentration of 96 per cent. A portion of the remainder is polymerized in the operation and passes into the raffinate stream.

Ammoniacal Copper Acetate (Butadiene). Butadiene is extracted commercially by an ammoniacal copper acetate solution (47). An eight-stage mixer-settler combination has been used, with the butanes-butenes-butadiene feed being charged to the fourth stage. Lean solvent enters at about 8°F and 45 psig, and about 8 lb of solvent are used per pound of feed. To provide reflux, rich solvent to the last stage is heated to 100°F to reduce its dissolving capacity and thus to reject a portion of the dissolved hydrocarbons. Butadiene product is fractionated from the solvent at a pressure of about 15 psig and a bottoms temperature of 175°F. Taken overhead as a vapor, the butadiene is washed with water to remove traces of solvent. The washed vapor is then compressed into a fractionator, where it is fractionated in the presence of a "flux oil" to produce a product of at least 98.5 per cent purity. Typically, 98 per cent of the butadiene is recovered.

Other Solvents. Many other solvents have been reported in the literature. Among the more unusual are sulfur dioxide–boron trifluoride, which is very selective for sulfur compounds and aromatics (2); hydrogen fluoride–silver fluoride, which is very selective for the extraction of aromatics (43); and hydrogen fluoride–boron trifluoride, which extracts alkylbenzenes, isomerizes the alkyl groups to 1,3, and 1,3,5 configurations preferentially, and may disproportionate the molecules (39,42).

Design of Extractors

Because the problems in the design of extraction equipment are basically the same as in distillation, the techniques of calculation are similar. First, it is necessary to decide how sharp the separation should be, then to choose optimum operating conditions to attain that separation, and finally to size the equipment. Because the selection of the optimum degree of separation often depends on the results of the subsequent calculations, several trial-and-error solutions may be required.

Criteria of Separation. When one is dealing with individual components, setting the criteria for separation is easy. In the extraction of butadiene, for example, the criteria are the recovery and the purity of the product. The situation is much less clear-cut, however, when dealing with such stocks as kerosenes, charge stocks to cracking, or lubricating oils. All of these are composed of a large number of components with varying degrees of affinity for the solvent, and it is not possible to specify the actual composition of the product. In such systems, the quality of a product is expressed in terms of some physical property, such as specific gravity, refractive index, or viscosity-gravity constant,* and equilibria data are expressed in terms of such properties. Ordinarily, it makes little difference which property is specified because they are all related (26).

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* Viscosity-gravity constant is defined by

$$\text{Viscosity-gravity constant} = \frac{10G - 1.0752 \log (V - 38)}{10 - \log (V - 38)}$$

where G = specific gravity 60°/60°F

V = Saybolt viscosity at 100°F, sec

Virgin distillates from the same crude usually have the same viscosity-gravity constant.

Temperature and Pressure. The first operating conditions to be set are extraction temperatures, which determine the selectivity of the solvent and its capacity for extraction. How temperature affects the selectivity of sulfur dioxide is illustrated in Fig. 4-15. Because contacting efficiency is better at higher temperatures and because entrainment is sometimes reduced, the optimum temperature may lie above the point indicated by equilibrium relationships (24). In treating lubricating-oil stocks, temperatures must be high enough to avoid the precipitation of wax. Determining the optimum extraction temperatures for a given application may be a very complex problem. Usually, they are set on the basis of experience.

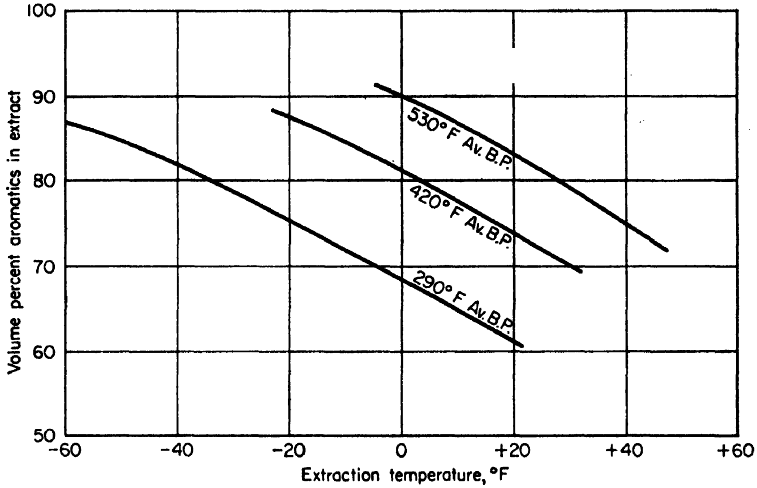

FIG. 4-15. Effect of temperature on concentration of aromatics in extract (74).

Extraction pressure must be high enough to hold feed and solvent in the liquid phase.

Solvent Rate, Stages, and Reflux. With temperatures set, the sharpness of separation depends upon the amount of solvent circulated, the number of countercurrent stages, and the amount of reflux employed. These may be specified on the basis of experience or of experimental data (64), or they may be determined by calculation if sufficient equilibria data are available. The calculation methods are similar to the methods used for distillation (50,67,70), but equilibria data have been published for only a few systems. In commercial extractions, seven equilibrium stages (exclusive of reflux stages) are often optimum (60) and more than ten are seldom used (45).

A semiempirical method for determining solvent and stage requirements in an unrefluxed system has been described by Gester (26). First, the yield obtainable by adsorption is determined, and the raffinate yield in solvent extraction is estimated from an empirical correlation. With this estimated yield and a small amount of experimental data, the solvent requirement and the material balance are calculated from mathematical relationships proposed by Kalichevsky (36).

The next step is to translate the theoretical-stage requirement into equipment requirements. Unfortunately, there are no generalized correlations, and data on the specific systems are usually required. Some laboratory data are available on packed columns (25), and operating data for 47 commercial units have been published by Morello and Poffenberger (45). For a packed column, contacting efficiency increases with throughput until the capacity of the column is reached.

Mixer-settlers constitute the safest design, inasmuch as each stage is equivalent to 75 to 90 per cent of a theoretical stage, independent of the size of the equipment or the materials contacted (45). This constancy presumes that sufficient power is supplied for mixing, although no method for determining how much is needed has been published. Correlations of power requirements have been published (59,60,61) for specific systems in rotating-disc contactors. In this type of unit, contacting efficiency increases with power input, as might be expected. Commercial units have been designed with an HETS (height equivalent to a theoretical stage) of about 3 ft. Comparisons are made with packed columns, but the details of the packed columns are not given.

Sizing. For the sizing of extraction columns, correlations have been proposed for packed columns (8) and rotating-disc contactors (59,60,61). Because of uncertainties in the correlations, Gester recommends a safety factor of 1.75 in the sizing of packed columns (26). Rotating-disc-contactor (RDC) correlations are not general, but apply only to the specific systems tested. The capacity of an RDC unit is reduced as power input is increased to improve contacting efficiency.

For other contactors, operating data should be referred to whenever possible. The tabulation of Morello and Poffenberger (45) is recommended.

For furfural operations in packed columns, charge rates are reported to average about 35 gal of oil per hr per sq ft of cross-sectional area, although rates as high as 70 gal/sq ft/hr have been observed (26).

ADSORPTION

Adsorption is a process in which a solid material is used to remove one or more components from a liquid or gas stream, without chemical reaction. Related processes have been used for many years to remove gum-forming materials from gasoline and colored materials from lubricating oils;* however, these processes involve chemical reactions. True adsorption processes have been developed only in recent years, and so far, they have not been used extensively in petroleum refining. Only the true adsorption processes will be considered in this chapter.

Principles of Adsorption

Just as certain liquids have different affinities for different hydrocarbons, so also do certain solids. If a hydrocarbon mixture, liquid or gaseous, is contacted with such a solid, certain of its components will concentrate on the surface; this effect makes separation possible.

Adsorbents. Because adsorption is a surface phenomenon, probably only one molecule deep, a practical adsorbent must be highly porous; a typical surface area is 80 acres per lb (68). In the adsorption of liquid, only small particles may be used because larger particles (larger than about 14 mesh in the case of silica-alumina) tend to fracture in a cyclic adsorption operation (21).

Most adsorbents attract hydrocarbons in the descending order: aromatics, olefins, naphthenes, and paraffins. Sulfur-containing materials are attracted about as strongly as aromatics.

Among the practical adsorbents are silica gels, silica-aluminas, activated aluminas, and activated charcoals. Silica gels are the most selective, silica-aluminas the least (21). Activated charcoals have the greatest capacities, silica-aluminas again the least. On the other hand, silica-alumina particles have a low tendency to fracture in adsorption operations.

Inasmuch as there are no normally gaseous aromatics, the adsorption of light hydrocarbons is primarily a function of volatility (23), although olefins are adsorbed somewhat more strongly than paraffins. Activated charcoals are recommended for separating light hydrocarbons (5,23). By way of comparison, the atmospheric-pressure capacity of charcoals for ethylene may be ninetyfold greater on a weight basis than the capacity of an absorption oil (5).

A new class of adsorbents that may become quite important in petroleum refining are molecular sieves (51). Consisting of synthetic zeolites, these adsorbents have pore openings of a uniform size—4 or 5 A in diameter, for example. The openings in 5-A sieves are small enough to preclude passage of all but straight-chain hydrocarbons. Thus, these sieves provide a new tool for separating straight-chain compounds from mixtures. As regards their external surfaces, molecular sieves have normal relative attractions for the various hydrocarbons, but the ratio of external to internal surface is small.

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* These operations are usually termed "clay treating." They are covered in Chap. 13.

The diffusion rate, or the rate of transfer of materials between the liquid and solid, is an important property of adsorbents. Because their diffusion paths are shorter, transfer rates are higher in smaller particles. Transfer rates are also higher in particles with larger pores, but these have lower surface areas and therefore lower adsorption capacities. Some materials have macropores that provide free access to micropores; such materials have high transfer rates as well as high capacities (21).

In addition to high capacity, high selectivity, high diffusivity, and resistance to fracturing, other desirable features include high bulk density, low pressure drop, ready desorption, low cost, and long life. Inasmuch as several of these properties conflict, the best adsorbent represents a compromise of desirable properties.

Temperature. Both the capacity and the selectivity of an adsorbent increase as the temperature is reduced, but the rate of transfer decreases. One rule of thumb (68) is to operate at the lowest convenient temperature, except when processing liquids whose viscosities would exceed 0.65 centipoise. With such liquids, higher temperatures are used to reduce viscosity to that point, or the liquid is diluted with pentane or butane.

Staging. For satisfactory separations, multistage units are usually required. Staging can be obtained by countercurrent flow of feed and adsorbent through a column. Practical considerations, however, limit this approach to the adsorption of gases. With liquids, the linear-velocity limitations for countercurrent flow would be too low to be practical (20). Fixed-bed adsorption is used, therefore, with liquid feeds. Staging is inherent in a fixed bed, inasmuch as the composition of the liquid changes continuously as it passes through the adsorbent bed.

Desorption. An adsorbate may be desorbed by heating the rich adsorbent in the presence of a flowing gas or liquid "strippant." Also, by virtue of the mass-action principle, an adsorbate may be displaced by a material that is equally attracted to the adsorbent. For example, benzene may be displaced by xylenes, and vice versa.

When gaseous hydrocarbons are processed, the adsorbate is volatilized into a hot stripping gas. Because vaporization of heavy adsorbate is difficult and because some polymerization of olefins or diolefins may occur, periodic treatment of the adsorbent at high temperatures may be required to prevent the accumulation of heavy materials (23). When liquid hydrocarbons are processed, impurities such as water, organic acids, and nitrogen bases are difficult to desorb. To avoid difficulties with these materials, the feed may be pretreated in guard chambers to eliminate them (19).

Adsorption Processes

Although there have been few commercial applications of true adsorption in the petroleum industry, four processes have been developed:

Hypersorption, fluid-char adsorption, cyclic adsorption, and Arosorb. Also Rotosorption is being used in the natural-gas industry, and molecular-sieve processes will probably be developed.

Hypersorption. Hypersorption (40*a*) separates light gases—hydrogen, methane, acetylene, ethylene, ethane, propene, and propane—from their mixtures. As shown schematically in Fig. 4-16, Hypersorption is much like reboiled absorption, with a downward-moving bed of charcoal substituted for lean oil. Hot, regenerated charcoal enters at the top of a column and passes down through a cooling zone countercurrent to a "purge gas," where the charcoal is dried and brought down to adsorption temperatures. From the cooling zone, the charcoal passes into an adsorption section, where it picks up the heavier components preferentially from the countercurrent feed stream. Below the feed, lighter components are displaced by a rising stream of heavier components in a stripping section. In the lowest zone, the charcoal is heated to about 500°F in the presence of counterflowing steam, which drives the adsorbate off the charcoal. Steam and bottoms product are withdrawn from just

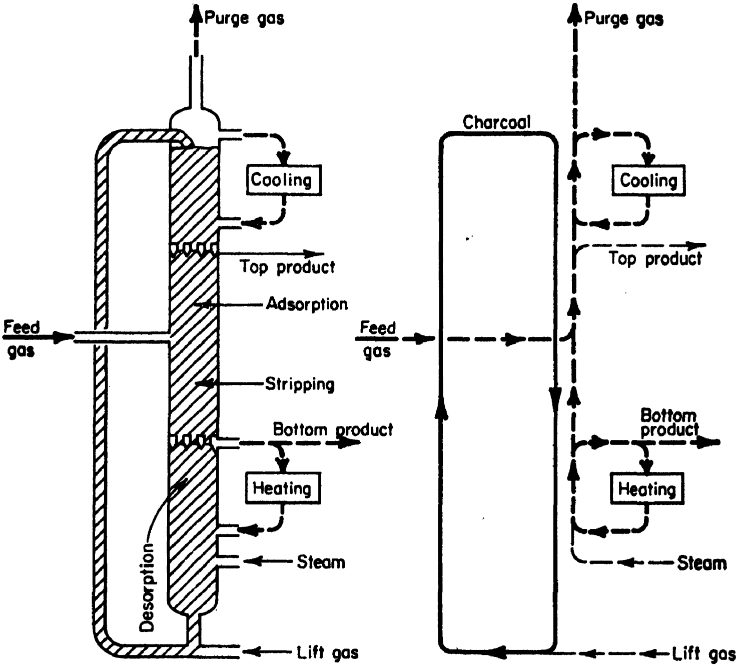

FIG. 4-16. Hypersorption column. NOTE: Operation of the intermediate portion of the column is similar to the operation of a reboiled absorber, except that a solid adsorbent replaces the liquid absorbent. The upper portion of the column is a cooling zone. In the lower portion of the column, the adsorbate is stripped off the charcoal; in absorption, the analogous operation is performed in a separate column.

Table 4-6. Typical Separation in Hypersorption (54)

Component	Compositions, vol %			
	Feed gas	Bottoms	Overhead	Purge gas
Hydrogen	39.8	.....	31.6	61.8
Nitrogen	1.7	.....	1.4	2.5
Carbon monoxide	0.9	.....	0.8	1.3
Oxygen	0.1	0.1	0.1	0.2
Methane	51.3	.....	66.1	33.7
Carbon dioxide	0.2	2.9	.....	0.1
Acetylene	0.2	3.6		
Ethylene	5.8	92.7	.....	0.4
Ethane	Tr.	0.7		
Total	100.0	100.0	100.0	100.0

below the stripping section, top product from just above the adsorption section. A portion of the purge gas is compressed for use as "lift gas," which picks up charcoal at the bottom of the column and carries it to the top. To avoid build-up of heavy materials on the circulating adsorbent, a small slip stream is circulated through a reactivator (not shown), where it is heated to a high temperature as heavy ends are stripped off with steam. Because of the high selectivity of charcoal, a gas stream can be separated into carbon-number cuts in a single tower by taking off sidestreams at suitable points. A typical separation is given in Table 4-6.

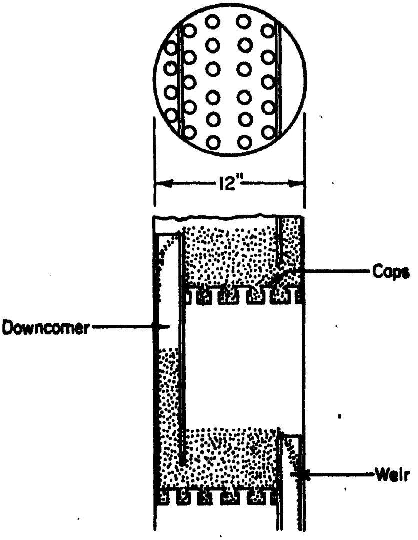

FIG. 4-17. Section of fluid-char adsorber (23).

Fluid-char Adsorption. Basically, fluid-char adsorption performs the same function as does Hypersorption. It differs in that a finer solid is used—a solid so fine that it flows like a liquid in the presence of an upflowing gas.* Accordingly, the charcoal is handled in a column just as a lean oil would be, and bubble-cap trays are used for contacting. A sketch of a fluidized-charcoal column is shown in Fig. 4-17. Advantages claimed (23) for the process include a small inventory of adsorbent, high heat-transfer coefficients for indirect heating and cooling of the

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* The principles of fluidized solids are discussed in Chap. 5.

adsorbent, small column volumes, and direct heating of charcoal with combustion gases in the reactivation step. Promising applications are stated to be separation of ethane and heavier gases from lighter gases, purification of hydrogen, concentration of acetylene, and recovery of traces of solvent vapors.

Cyclic Adsorption. Cyclic adsorption separates liquids by chemical type. Probably its major utility will be in the separation of aromatics from hydrocarbon mixtures, although olefins (20) and sulfur compounds (19) can also be separated. Inasmuch as moving beds are not feasible in liquid-phase adsorption (20), feed is passed over fixed beds of adsorbent, and adsorbate is stripped off the adsorbent subsequently by a hot liquid strippant. To simulate counterflow of adsorbent to the flow of feed and strippant, each of the liquid streams passes through several beds of adsorbent in series, and the beds of adsorbent are so piped that they can be used cyclically in any position. Thus, the beds can be made to "move" countercurrent to the flow of liquid feed and strippant.

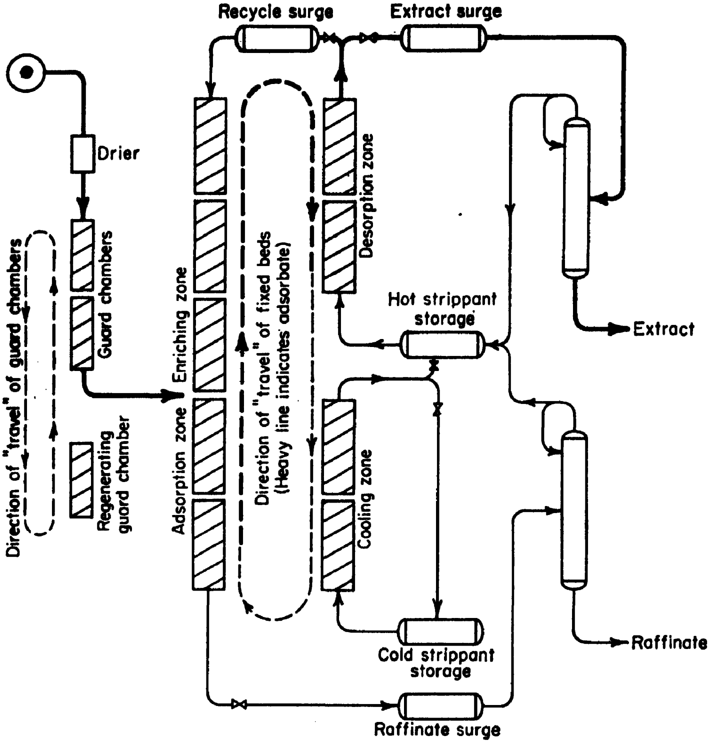

FIG. 4-18. Schematic diagram of cyclic-adsorption unit.

A typical flow pattern for separating aromatics is shown in Fig. 4-18. Regenerated adsorbent "passes" countercurrent to the feed in an adsorption zone, where aromatics are adsorbed, together with some nonaromatics. The adsorbent "carries" the adsorbate (and interstitial liquid) into an enriching zone, where it is contacted with a countercurrent recycle stream. The recycle stream, consisting of a paraffinic strippant and aromatics, displaces nonaromatics in the bed. From the enriching zone, the rich adsorbent passes into a desorption zone, where it is contacted with hot strippant liquid at 200 to 250°F to desorb the aromatics. Immediately after each bed of adsorbent is transferred to the desorption zone, the first increment of effluent is rich in strippant; this increment is recycled back to the enriching zone. The rest of the effluent is sent to an extract fractionator to separate strippant from the aromatic product. Raffinate is also fractionated to recover strippant introduced via the recycle stream. To complete the adsorbent cycle, hot adsorbent beds from the desorption zone are cooled by circulation of cold strippant. The

Table 4-7. Typical Cyclic Adsorption Operations (19,20)

	Catalytic reformate	Kerosene	Catalytic cycle oil	Cracked gasoline	Dearomatized cracked gasoline	Cracked gasoline
Charge stock:						
Aromatics, vol %	35.8	22.5	40	19	......	20[a]
Bromine no., g/100 g	3	0	9	71	55	71
Sulfur, wt %	......	......	......	......	......	1.22
ASTM 10% off, °F	206	396	465	230	240	230
ASTM 90% off, °F	269	474	590	354	350	354
Strippant	Pentane[b]	*i*-octane	*i*-octane	Pentane	Pentane	Pentane
Adsorbent	← 28–200-mesh silica gel →					
Feed/gel, gal/lb	← 0.05–0.10 →					0.091
Recycle/feed, gal/gal	2.27	1.02	1.74	1.28	2.4	1.1
Strippant/feed, gal/gal	4.7	2.6	5.5	4.9	5.2	4.0
Cycle time, hr	1	3	0.75	0.75	0.75	1
Raffinate:						
Yield, vol %	65	76	59	78	53	67
Bromine no	4	0	0	55	1	57
Sulfur, wt %	......	......	......	......	......	0.03
Extract:						
Yield, vol %	35	24	41	22	47	
Aromatics, vol %	99.8	92	95	87		
Bromine no	1	0	20	80	117	85
Sulfur, wt %	......	......	......	......	......	3.5

[a] Aromatics plus sulfur compounds. [b] Dearomatized kerosene also used.

first portion of the strippant from any bed is hot; it is sent to hot-strippant storage. Cooled adsorbent beds "pass" to the adsorption zone.

Because polar materials, such as water, organic acids, and nitrogen bases are difficult to desorb, the feed is dried and then pretreated to keep such materials out of the main adsorbent beds. Pretreatment consists of passage over adsorbent guard chambers, which are periodically regenerated by displacement with ethyl alcohol. The alcohol is recovered by stripping the adsorbent with hot pentane vapors.

In pilot-plant operations, aromatics were separated from nonaromatics with 28–200 mesh and with 48–80 mesh silica gel at superficial velocities as high as 250 gal per hr per sq ft of column cross section (19). Cycle times ranged from 20 to 60 min. Some typical operations are shown in Table 4-7.

When high-purity products are not required, fewer adsorbent beds are required. For removing aromatics from kerosenes, for example, three beds might suffice (29).

Table 4-8. Investment Costs and Utilities for Cyclic Adsorption (35)

	Aromatics recovery			Kerosene refining		
Utilities/1,000 bbl per day of feed:						
Power, kw	104			2.32		
Fuel, 1,000,000 Btu/hr	18.5			2.97		
Steam (150 psig), lb	....			2,230		
Steam (15 psig), lb	....			650		
Cooling water (90°F), gpm	905			300		
Metal requirements, bbl per day	2,000	4,000	8,000	3,500	7,000	10,000
Steel, short tons	1,600	2,200	3,200	1,000	1,400	1,900
Admiralty and brass, short tons	17	33	65	4	8	12
Investment (1953), dollars/bbl per day of charge	750	500	375	260	190	170

Utilities requirements for two typical operations are shown in Table 4-8, together with estimates of steel requirements and investment costs (29). Operating costs for recovering aromatics were estimated (in 1949) to be 1 to 3 cents per gal of feed for plants processing 2,000 to 15,000 bbl per day (20).

Arosorb. Like cyclic adsorption, the Arosorb process (68) separates aromatics from nonaromatics; it differs from cyclic adsorption in the technique used for desorption. An aromatic material with a boiling range different from that of the feed is used to displace the aromatic product.

Let us consider the separation of benzene from a hexane stream, with xylenes used as the desorbent. As the cycle begins, the adsorbent is saturated with xylenes. Dried benzene concentrate is passed through the bed, the benzene displacing the xylenes, which pass out with raffinate hexanes. When the benzene-xylene interface approaches the outlet end of the bed, the feed is diverted to another adsorbent bed. A paraffinic "push liquid," such as butane, is then passed through the benzene-saturated adsorbent to displace hexanes adsorbed or in the interstices of the bed. Push liquid is followed by desorbent xylenes, which displace the benzene and the push butanes to complete the cycle. How the effluent from such an adsorbent bed changes is shown in Fig. 4-19. A mixture of xylenes and hexanes comes through first, followed by a mixture of xylenes, hexanes, and butanes, together with a trace of benzene. As the hexanes disappear from the effluent, the concentration of benzene rises sharply. By choice of the proper cut point, the effluent can be divided into two streams, one containing most of the hexanes, the other containing most of the benzene. Both streams contain push butanes and desorbent xylenes, from which they are separated by distillation. For maximum recovery and purity, the cut point is sharpened by recycling a cut-point fraction back to the Arosorber feed. A schematic diagram of an Arosorb unit is shown in Fig. 4-20.

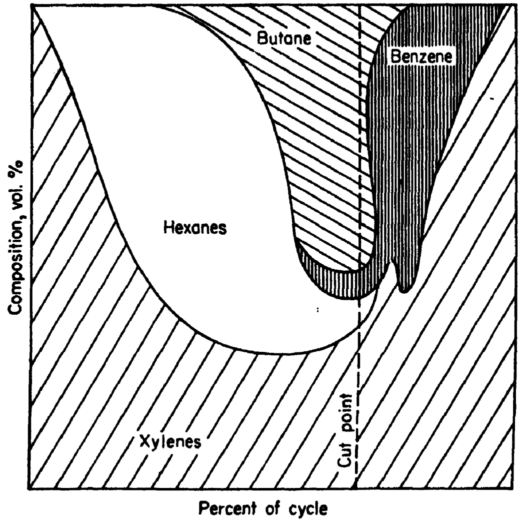

FIG. 4-19. Effluent from a typical Arosorb operation.

If high-purity products are not required, push liquid can be eliminated from the cycle, with a considerable reduction in operating cost. In such a case the desorbent is a mixture of aromatics and nonaromatics, the latter taking the place of the push liquid.

For sizing an Arosorb bed, a flow rate of 0.4 gpm of fresh feed per square foot of cross section is recommended (68). Operating costs were indicated to be 1 cent to 3 cents per gal of charge in 1953.

Rotosorbers. Rotosorbers (52) consist of cylinders of adsorbent arranged vertically on a turntable inside a high-pressure drum. As the turntable revolves, the adsorbent cylinders pass successively over feed, strippant, and purge ports. Few details of the operation have been published.

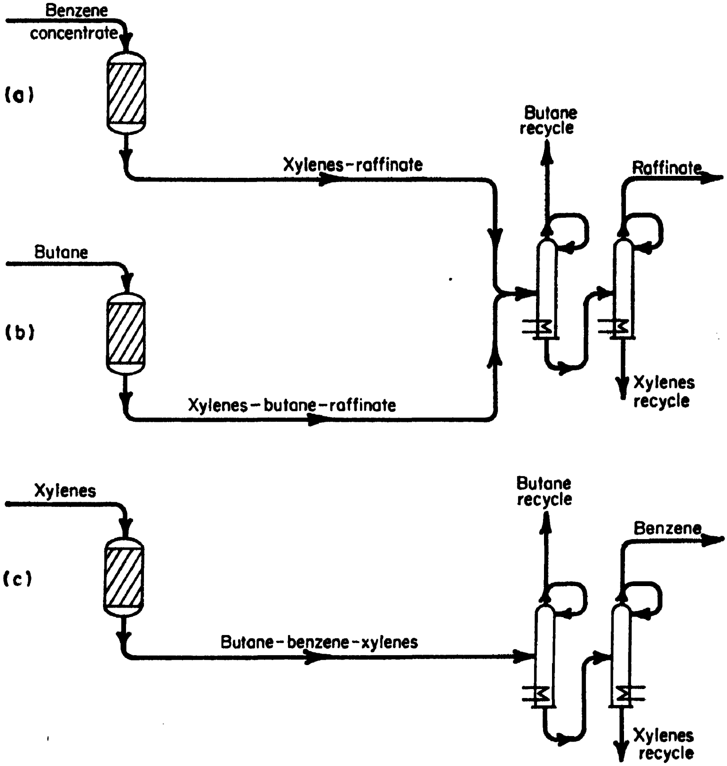

FIG. 4-20. Production of benzene by Arosorb process. (*a*) First step: As this case goes on stream, the silica gel is saturated with xylenes. Benzene in the feed replaces the xylenes, which pass out in the raffinate. The operation is continued until the benzene-xylenes interface approaches the outlet end. (*b*) Second step: Butane displaces the benzene-boiling-range nonaromatics from the interstices of the bed and from the adsorbate, leaving butane and benzene and some xylenes in the case. (*c*) Third step: Xylenes displace butane and benzene from the case. Some xylenes pass through into the butane-benzene stream.

Molecular Sieves. Molecular sieves have potential applications wherever the separation of normal paraffins is desirable (76). Because molecular sieves have strong affinities for polar compounds, such as water, hydrogen sulfide, or carbon dioxide, they may also be used to separate these materials from gaseous or liquid hydrocarbons (55). Normal olefins may also be separated from other hydrocarbons.

CRYSTALLIZATION

Crystallization is one of the earliest refining processes. It was first practiced inadvertently when wax crystallized out of crude oil in winter storage. Wax boils in the lubricating-oil range and is often an undesirable constituent in such oils. Consequently, when the market for lubricating oils became important, processes were developed to employ this separation principle effectively. Crystallization has also been applied to separate *p*-xylene in high purity from petroleum stocks, particularly from xylene extracts separated from catalytic reformates. *p*-Xylene is a raw material in the manufacture of Dacron polyester fiber.

Principles of Crystallization

It is well known that the freezing point of a liquid is lowered by the addition of a second, miscible liquid. Let us consider what happens if two liquids, say *p*-xylene and *m*-xylene, are mixed in various proportions. Pure *p*-xylene freezes at 56°F. As *m*-xylene is added, the freezing point of *p*-xylene drops along the line *AB* of Fig. 4-21. Similarly, *m*-xylene freezes at −54°F, and as *p*-xylene is added, its freezing point drops along the line *CD*, intersecting *AB* at *E*. Now let us consider the cooling of a solution of composition *F* from temperature T_1. Nothing happens until

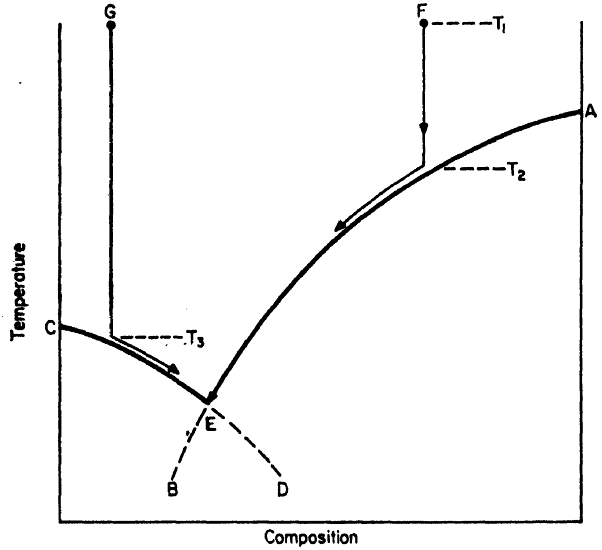

FIG. 4-21. Typical freezing-point diagram.

the temperature reaches T_2; then, *p*-xylene begins to crystallize out. As cooling continues, the temperature and composition of the remaining liquid follow the line *AB*. Similarly, when starting with composition *G*, crystallization of *m*-xylene begins at temperature T_3, and the temperature and composition of the remaining liquid follow the path *CD*. In either case, both xylenes crystallize out together when composition *E* is reached, and the crystals are of the same composition as the liquid. This composition is called the "eutectic" for the binary system. It is obvious from the diagram that only one material can be crystallized in pure form out of a given mixture, and the recovery of that component is limited by the composition of the eutectic.

Because the crystals formed in the process trap liquid, it is not possible to obtain a pure product in one stage. Melting and recrystallization are often used for purification.

Crystallization Equipment

The basic equipment in crystallization consists of chillers, in which the feed is cooled by indirect heat exchange, and filters for the separation of the crystals from the remaining liquid. Because the crystals tend to adhere to the walls of the chillers, scraped-surface exchangers are used.

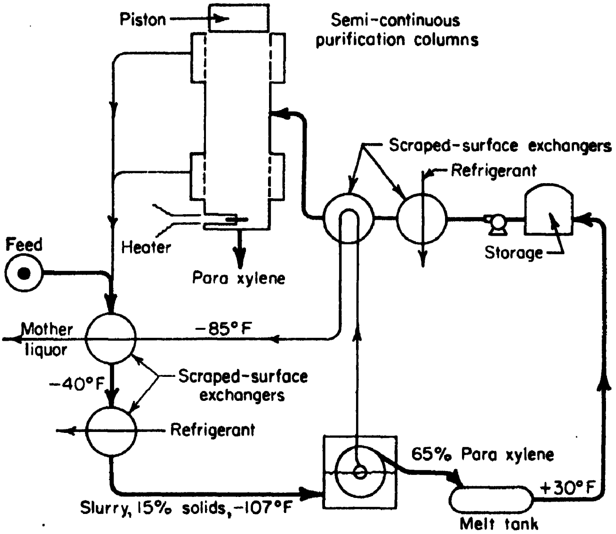

FIG. 4-22. Recovery and purification of *p*-xylene by crystallization.

For recrystallization, semicontinuous purification columns have been designed (11). As illustrated in Fig. 4-22, each column includes a piston that compresses the crystals and forces entrapped liquid out through filters built into the column walls. An electric pancake heater at the bottom of the column melts the product, most of which is taken off as a liquid. The rest passes up the column as "reflux" to displace impurities in the crystals.

Crystallization Operations

Dewaxing is basic to the manufacture of lubricating oils; it is discussed in Chap. 11. A flow sheet for the production of *p*-xylene is shown in Fig. 4-22. Closely-fractionated xylenes, containing about 17 per cent *p*-xylene, are mixed with recycle *p*-xylene and chilled in scraped-surface exchangers to −107°F, which is close to the eutectic temperature. Effluent from the chillers contains about 15 per cent solid crystals, which are filtered out in a rotary filter and charged to a melt tank held at about 30°F. Because liquid is trapped in the crystals, the melt contains only about 65 per cent *p*-xylene. The melted xylenes pass through storage to secondary chillers which cool them to 0°F, thus producing a thick slurry resembling soft ice cream. The slurry then passes into one of two semicontinuous purification columns. Reject liquor containing about 40 per cent *p*-xylene is taken off the sides of the columns through filters and recycled to the feed chillers; recycle constitutes about 10 per cent of the total feed. *p*-Xylene of 98 to 99 per cent purity is recovered in a yield of 75 per cent. Yield is limited by the eutectic compositions of *p*-xylene, the *p*-xylene-lean "mother liquor" containing about 6 per cent *p*-xylene.

OTHER SEPARATION PROCESSES

Other separation processes which are of interest in petroleum refining include thermal diffusion, rotary distillation, molecular distillation, gas chromotography, and clathration. Although some of these have been used extensively as analytical tools, none of them has, as yet, been applied commercially in petroleum refining.

Thermal Diffusion

From a theoretical standpoint, thermal diffusion is probably the least understood of separation processes. It depends upon the use of a narrow passage between a hot and a cold surface. When mixtures of certain liquids are passed through such a passage, some of the components concentrate along the hot surface, some along the cold surface (31,32,34,35), and this phenomenon makes separation possible. Separation results from differences in molecular shape (33,73). The hot and cold surfaces may be parallel plates or cylinders forming a narrow annulus. Typical annuli range from 0.01 to 0.15 in. A liquid-permeable membrane that divides the passage into two narrower ones improves the separation (35). In Table 4-9, separations that have been effected are tabulated, together with some that have not worked out. A theory for the thermal diffusion

Table 4-9

Liquid Mixtures Separated by Thermal Diffusion

Mixture	*Reference*
Benzene, carbon tetrachloride	35
Benzene, cetane	35
Benzene, *n*-heptane	35
Benzene, methylcyclohexane	35
Benzyl alcohol, ethylene glycol	35
Carbon tetrachloride, cetane	35
Cetane, cumene	35
Cetane, monomethylnaphthalene	35
Cetane, toluene	35
Cetane, *m*-xylene	35
Chlorobenzene, toluene	35
Cumene, methylnaphthalene	35
Cumene, methylcyclohexane, *n*-octane	35
Cyclohexane, 2,4-dimethylpentane	35
Cyclohexane, toluene	35
Cylinder stock	31
1,2-Dimethylcyclohexane, cis- and trans-	35
Fish oils	31
Gas oils, catalytic	31
Gas oil, virgin	31
n-Heptane, methylcyclohexane	35
i-Octane, methylcyclohexane	35
i-Octane, *n*-octane	35
i-Paraffin, naphthenes	31
Kerosene	31
Lubricating oil	31
Methylnaphthalene, alpha- and beta-	35
Paraffin distillate	32
Paraffin-distillate extract	32
Paraffin-distillate raffinate	32
Paraffin, xylenes	35
Slack wax	31
Solvent-extracted oil	31
Tall oil	31, 34
Vegetable oil	31
o-Xylene, *m*-xylene	35
o-Xylene, *p*-xylene	35
4-Thiaheptane, thiacyclohexane	72

Liquid Mixtures Not Separable

Benzene, cyclohexane	35
Cetane, cyclohexane	35
Methylcyclohexane, toluene	35
m-Xylene, *p*-xylene	35
Thiacyclohexane, benzothiophene	72

of liquids has been proposed, which gives qualitative agreement with observed phenomena (17). High heat requirements make the commercialization of thermal diffusion difficult (73).

Rotary Distillation

Rotary distillation equipment consists of a heated shell enclosing a cooled rotor; the annulus between the two is only about 1 mm thick. As vapor moves up the column, it condenses on the cooled rotor; condensate is thrown off by centrifugal force and is reevaporated on the heated shell. The number of equilibrium stages increases as throughput is reduced. As many as 500 theoretical plates have been obtained in a unit 5 ft long and 5 in. in diameter (7).

Molecular Distillation

Molecular distillations are conducted under very high vacuums—of the order of 0.001 mm Hg. Under such low pressures, materials behave as though in a perfect vacuum. Since there is substantially no back pressure, there is no vapor pressure and no equilibrium. Separation depends on differences in evaporation rates; evaporation rate depends on molecular weight. In commercial units, feed is charged to the apex of a heated wide-angle cone rotating at high speed. Rotation spreads the feed out into a thin film, which provides a large surface for evaporation. Commercially, molecular distillation is applied to the separation of heat-sensitive materials, such as fish and vegetable oils and vitamins.

Gas Chromatography

Although gas chromatography was not developed until about 1955, it has become an important tool for analyzing light hydrocarbons. The operation is carried out by introducing a small liquid sample at the top of a column of adsorbent and then passing a stream of fixed gas, such as nitrogen, through it. The fixed gas carries the various components through the bed at different rates. Thus, each component comes out in the effluent at a different time. Measurement of some physical property of the changing effluent—gas density or thermal conductivity, for example—provides information from which the analysis of the original sample can be calculated.

Clathration

Clathration separates hydrocarbons by forming complexes of the feed components with inorganic materials; different hydrocarbons have different tendencies to form such complexes. Clathration was first disclosed in 1957 (30).

Permeation

Certain solid materials preferentially absorb specific liquids. Membrane permeation makes use of this property to separate such a liquid from a solution. The solution is passed on one side of a very thin membrane (0.001 in., for example), on the other side of which the pressure is reduced sufficiently that any material passing through the membrane is vaporized. Components that dissolve on the higher-pressure (liquid) side evaporate into the lower-pressure (vapor) space and are withdrawn as vapor. Membrane permeation was first disclosed in 1958 (*5a*). It can be used to separate water from various azeotropes—for example, from water-alcohol—and to resolve various hydrocarbon azeotropes. The principles of permeation are not well understood, and experimentation is required to determine whether any given system is susceptible to separation.

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CHAPTER 5

MOVING BEDS AND FLUIDIZED BEDS OF SOLIDS

Until about 1940, the handling of solids was a minor problem in petroleum refining. Clays had long been used for "finishing" petroleum products—by decolorizing, for example—but originally they were employed only in the form of fixed beds, through which the oil was percolated, or in the form of fines that were slurried into the oil and then filtered or centrifuged out. The advent of catalytic cracking in 1936 changed this picture. Because the solid catalysts had to be regenerated frequently by burning carbonaceous deposits at controlled temperatures, fixed-bed units were difficult to design and expensive to build. It soon became obvious that cheaper plants could be built if the catalyst could be circulated between a reaction vessel and a regenerator. Intensive work on the problem led to two early solutions—moving beds, commercialized in 1943, and fluidized beds, commercialized a year earlier. The development of these two systems opened up a wide range of applications, both within and outside the industry, and a large number of processes are now employing them. Included are gaseous reactions over solid catalysts, reactions between gases and solids, and even reactions between two solids (7).

Comprehensive discussions of the principles of moving and fluidized beds have been published by Zenz (48) and by Leva (22).

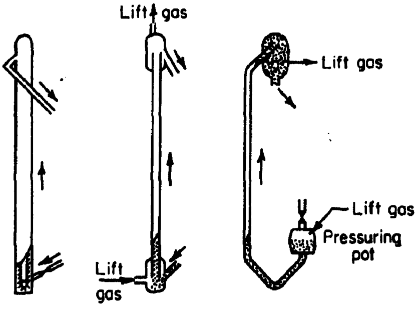
MOVING BEDS

As the name implies, a moving bed of solids consists of a packed bed that moves vertically through a vessel. The size of the individual particles is usually about ⅛ in. in diameter, but particles from 30–60 mesh to ¾ in. in diameter may be used (41,42,47). In all commercial applications thus far, moving beds have been downflow. However, movement can be upflow, and an upflow system has been installed in a semiworks shale-retorting unit (39). To reduce frictional resistance, the vessels of an upflow unit are designed with a small cross section at the bottom, the cross section increasing as the solids pass upward (3).

Principles of Moving Beds

That small particles of dry solids will flow when a force is applied is self-evident. Any force may be used, and gravity is usually the most convenient. However, the force of gravity can solve only half the problem; the solids must be returned to the tops of the vessels to complete the cycle. Other problems include obtaining uniform flows of solids across vessel cross sections, introduction of feed and removal of products, sizing of vessels, control of temperatures, and control of flow rates.

Conveying of Solids. The problems of elevating solids was first solved by use of expensive bucket elevators on endless chains.* Next, gas lifts were developed (41), in which high-velocity gas streams lift the solids through large lift lines. At the velocities employed, the solid particles separate into discrete units that are carried up individually.† The most recent system employs a gas stream, but in smaller volumes, and lift lines are so designed that the solids move upward in a compact mass.‡ In such systems, gas velocities are high enough to cause fluidization, but the movement of the bed is restricted at the upper end of the pipe so that bubbles of gas cannot form (48*d*). One means of providing this restriction is to flare out the upper part of the lift line to form a hopper with a diameter large enough to reduce the velocity of the lift gas below the velocity at which the solids would fluidize. The diameters of lift lines increase regularly from the bottom to the top (44). Such tapering reduces resistance to flow of solids, avoids increasing gas velocities as the gas flows up (and as frictional resistance lowers gas pressure), and facilitates control of flow rates (48*c*). Examples of the three conveying systems are shown schematically in Fig. 5-1, and their operating character-



(a) (b) (c)

FIG. 5-1. Methods of raising solids in moving-bed systems. (*a*) Elevator. (*b*) Gas lift. (*c*) Mass lift (hyperflow).

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* Originally two elevators were used. Later, a single elevator with compartmented buckets was developed. Each bucket has three compartments. The cooler solids are carried in the two outer compartments, the hotter solids in the middle one. This arrangement minimizes temperature problems with the sprocket wheels that carry the endless chains.

† In one instance 12,000 cubic feet (standard conditions) of 2-psig air were used per minute to transport 4.5 tons of cracking catalyst per minute (44).

‡ The original version of this "mass-lift" principle is called "Hyperflow"; it was developed by the Union Oil Company.

istics are compared in Table 5-1. Although all three systems are in use, elevators are seldom installed in new units.

Table 5-1. Comparison of Three Methods of Conveying Solids (3,37)

	Elevators	Gas lift	Mass lift
Velocity of solids, fps	0.3–2	15–40	10–12
Pressure differential required, psi	None	1–2	High
Amount of lift gas required	None	Large	Small
Investment cost	High	Low	Low
Usefulness at high temperatures	Poor	Good	Good
Usefulness at high pressures	Fair	Fair	Good
Rate of transport of solids, tons per hr	500 (maximum)	400 (27-in. line)	900 (12-in. line)

Flow of Solids. Because the solids-outlet port from a moving-bed vessel is considerably smaller than the vessel itself, there is a tendency for the solids to form a stagnant zone at the bottom of the vessel, around a cone of moving solids (29,48*a*).* In view of this tendency, a special mechanism is employed at the base of each vessel to maintain equal flow rates through its cross section. Two such mechanisms are illustrated in Figs. 5-2 and 5-3.

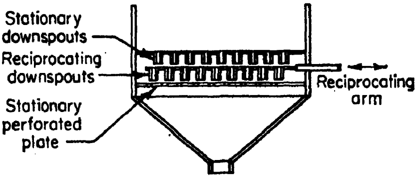

FIG. 5-2. Flow-control device for moving beds (3).

The design of Fig. 5-2 utilizes two horizontal plates, each equipped with cylindrical downspouts. The upper plate is fixed, and the lower plate moves back and forth. At one end of the stroke, the downspouts of the reciprocating plate are directly below those of the fixed plate, and solids drop through to fill the lower downspouts. At the other end of the stroke, the reciprocating downspouts are directly above holes in a fixed perforated plate, through which the solids discharge. Flow rate is controlled by frequency of oscillation.

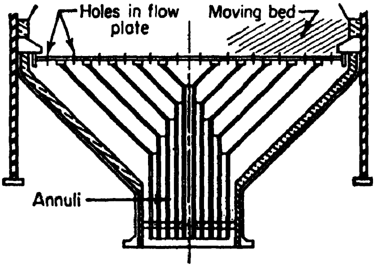

FIG. 5-3. Flow-control device for moving beds (41).

In Fig. 5-3, solids discharge through a horizontal perforated plate, with holes arranged in concentric circles. The solids then flow through con-

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* The angle formed by the slope of the cone (in comparison with the vertical) is called the "angle of internal friction"; it is usually close to the "angle of repose" and to the "angle of rupture" (48*a*).

centric cones and thence into carefully spaced vertical annuli that make up the discharge port. Sometimes a dished head with vertical downcomers is substituted for the horizontal perforated plate. Concentric-cone designs eliminate mechanical problems associated with earlier designs, which employed multiple perforated plates (41).

Feeds and Draw-offs. To distribute feed vapors across a moving bed and to withdraw product uniformly from it, special vapor trays have been devised. The same designs are used for both purposes, and three of them are shown schematically in Figs. 5-4 to 5-6. All three provide for passage of the moving bed past interconnected vapor channels, through which vapors are withdrawn or introduced.

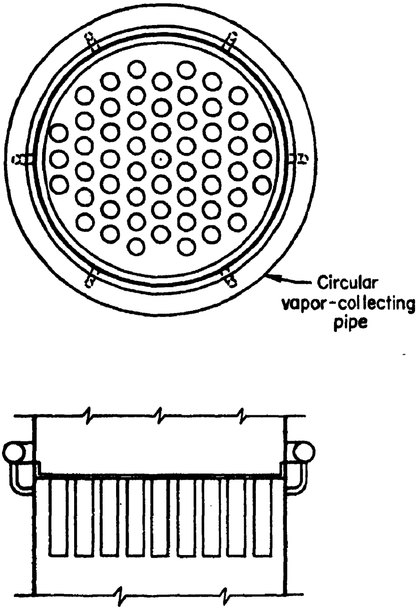

Fig. 5.4

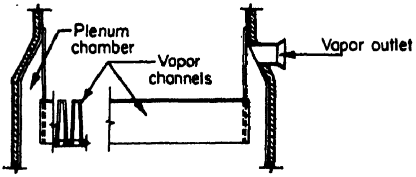

Fig. 5.5

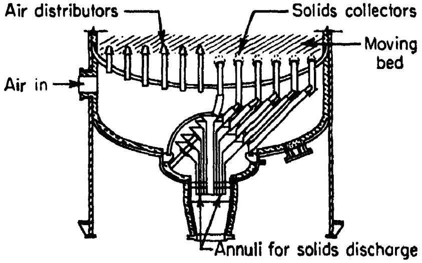

Fig. 5.6

Figs. 5-4, 5-5, and 5-6. Devices for withdrawing vapors from or introducing them into moving beds (3,41).

In Fig. 5-4, the vapor space may be likened to the shell side of a single-pass heat exchanger; the cylindrical downspouts for the solids correspond to exchanger tubes.

The version of Fig. 5-5 consists of inverted V-channels, each channel connecting with a central conduit through which vapors are withdrawn or introduced. Around the vapor tray, the tower is "coned out" to provide a plenum chamber. This feature avoids expansion problems inherent in earlier designs (41). To increase vapor-handling capacity, two sets of parallel vapor channels may be provided, one above the other.

The third design, illustrated in Fig. 5-6, is used in conjunction with the dished-head, flow-control device for solids which was mentioned earlier. It consists of cylindrical vapor risers that pass through the dished head, interspersed among the solids-draw-off downcomers. (To simplify the illustration, the risers are shown on only one side of the vessel, the downcomers on the other.)

Sometimes it is desirable to charge the feed stock as mixed liquid and vapor, for example, in catalytic cracking. In such cases, the feed is charged at the top of the vessel, and flows concurrent with the solids, but at a faster rate. The feed inlet must be designed to provide even distribution of the liquid on flowing solids. As shown in Fig. 5-7, distribution is accomplished by spraying the liquid feed onto a cylindrical falling curtain of solids (45). A manifold submerged in the catalyst entry zone is used alternatively (4).

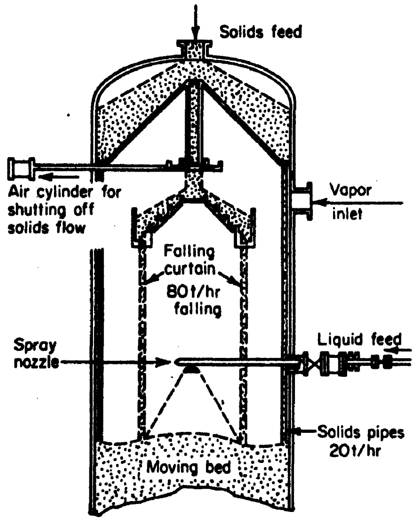

FIG. 5-7. Device for introducing liquid feeds into moving beds (45).

Vessel Sizing. Generally speaking, a given vessel volume is provided most economically by use of the smallest diameter possible. With an upward flow of gas, the minimum diameter is limited by the pressure drop of the flowing gas, which must be less than the head of solids (47). The usual equations for pressure drop through packed beds apply (23,24), with the velocity term equal to the relative velocity of gas and solids. However, application of these equations is difficult (probably because of the presence of fines, which result from attrition of the moving solids), and designers lean heavily on experience.

Smaller-diameter vessels are also advantageous from the standpoint of staging. The smaller the diameter, the greater the height for a given volume and the larger the number of contacting stages (3).

To avoid the use of large-diameter vessels, it is sometimes desirable to split the flow of gases and solids between two contacting sections (3). Although such a design is complicated, it should be cheaper to build than two parallel vessels.

Heat Transfer. In moving-bed operations, heat-exchange surface is often required to raise or lower temperatures, or to remove exothermic heat of reaction. The calculation of heat-transfer coefficients is difficult, and actual coefficients often differ from calculated ones; therefore, designs are usually based on experimental data and practical experience (47). Over-all coefficients are low; they range between 5 and 20 Btu/(hr)(sq ft)(°F). Heat transfer between the moving solids and gases in direct contact is rapid, and temperature equilibrium is quickly approached (29,32).

Flow Controls. Both vapor and solids must be flow-controlled in a moving bed. Vapor flows are controlled by pressure differentials. When two vessels are interconnected, seal legs and seal gas may be used to prevent vapor from passing between them. As illustrated in Fig. 5-8, seal gas is introduced to the seal leg in sufficient quantities that it flows in both directions and thus prevents other vapors from entering the seal leg (29). Because of seal-gas pressure drop, there is a pressure differential across the seal leg. In the original moving-bed units, with solids conveyed by elevators, seal legs were used to provide the "head" required for introducing solids from the top of the elevators, which operated at atmospheric pressure, to the reactors, which operated at higher pressures. Seal legs as long as 70 ft were employed for this purpose (42).

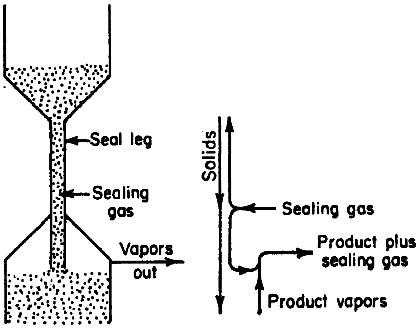

Fig. 5-8. Seal leg for moving beds.

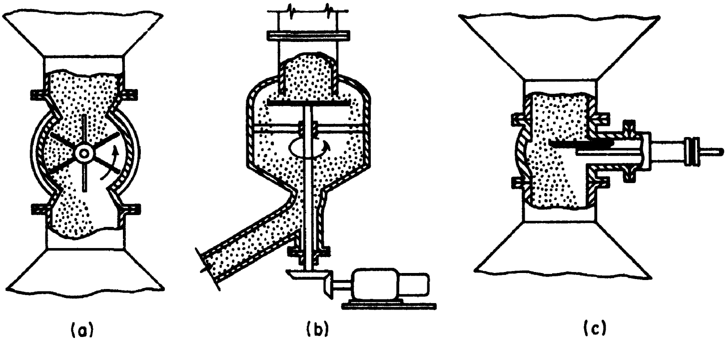

Fig. 5-9. Feeders for downflowing solids (3). (*a*) Star feeder. (*b*) Rotating-table feeder. (*c*) Slide valve.

For controlling the flow rates of downflowing solids, various devices have been employed, three of which—the star valve, rotating-table valve, and slide valve—are illustrated in Fig. 5-9. Contrary to expectations, the rate of solids flow is almost independent of the height of the moving bed when slide valves are used.

For upflowing solids, a piston-type feeder has been proposed. How it would operate is shown in Fig. 5-10.

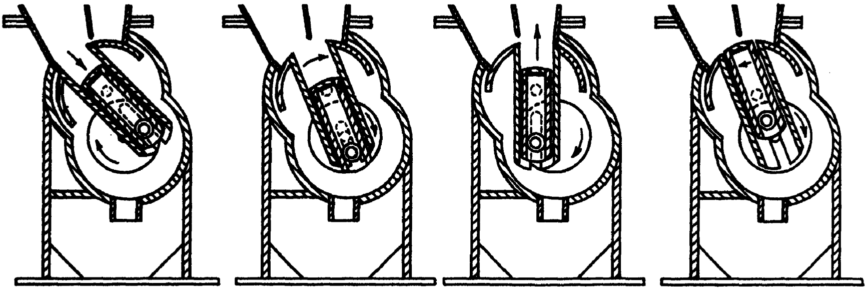

FIG. 5-10. Feeder for upflowing solids (3).

Vessel Arrangements

Moving-bed systems usually contain two major vessels, for example, a reactor and a catalyst regenerator. Originally, the vessels were set side by side, as illustrated in Fig. 5-11 for a catalytic cracking unit. Regenerated catalyst, elevated by the taller elevator, was dropped into a hopper and then through a seal leg, where counterflowing seal gas built up the pressure to the reaction pressure. From the seal leg, the catalyst passed into and through a reactor, where it contacted a concurrent feed stream.* Below the product-draw-off point, the catalyst was stripped with countercurrent steam; it then passed through another seal leg to an elevator which carried it to the top of the regenerator, where the flow process was repeated, except that stripping of the regenerated catalyst was not practiced and cooling coils were provided to remove the heat of combustion.

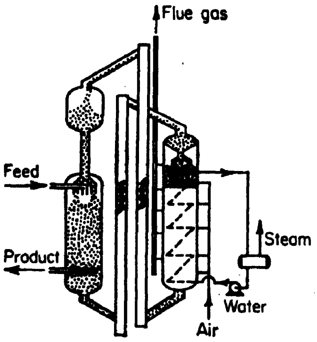

FIG. 5.11

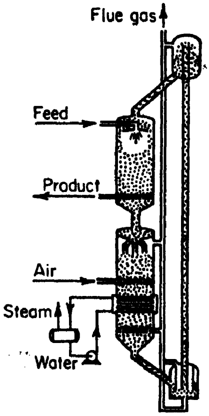

FIG. 5-12

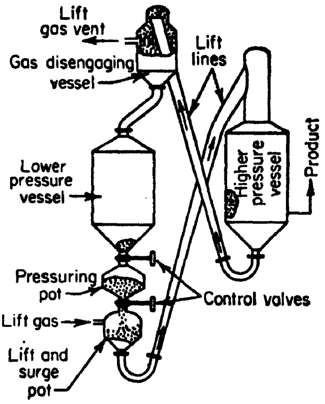

FIG. 5.13

FIGS. 5-11, 5-12, AND 5-13. Vessel arrangements for moving bed systems (3,42).

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* In the earliest units, the feed passed upward, countercurrent to the moving bed. With this arrangement, only completely vaporized feeds could be charged.

With the advent of the gas-lift and mass-flow methods for conveying solids, it became possible to place one vessel above the other (35). As shown in Fig. 5-12, the reactor (in catalytic cracking, at least) is usually placed on top. Except for the vessel arrangement, the design is the same as for the side-by-side unit.

When substantially different pressures are desired in the two vessels, the side-by-side arrangement has advantages in conjunction with the mass-lift system for conveying solids (3,19). As shown in Fig. 5-13, the large pressure drops across the lift lines permit holding the two vessels at different pressures. For transferring solids from the lower-pressure vessel to the higher-pressure vessel, a lock-hopper system may be used, as indicated on the diagram. A pressuring pot alternates between low and high pressures. When the pot is at low pressure, solids are transferred to it from the low-pressure vessel. The valve from that vessel is then closed, and pressure is raised. The valve to the high-pressure vessel is then opened, and solids are discharged through it. A pressuring pot can be operated without valves in the lines connecting it with the high-pressure and low-pressure vessels (19). As illustrated in Fig. 5-14, gas flows through the interconnecting piping are regulated to give the desired pressure differentials between the vessels.

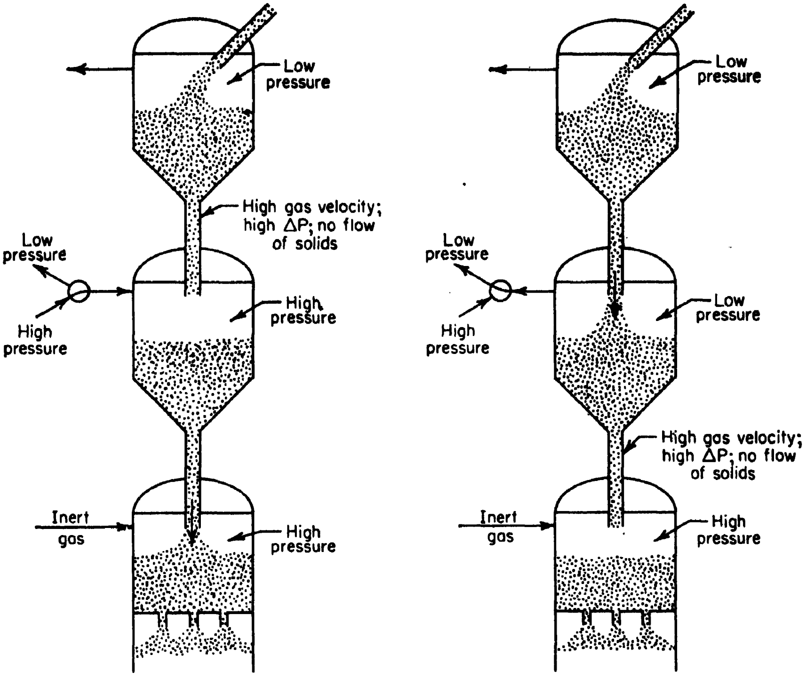

FIG. 5-14. Operation of pressuring pot without valves in solids flow lines.

Mechanical Problems

In the original moving-bed units, maintenance of the elevators was a major problem; wear was especially severe on the upper sprockets, which operated in a hot, dusty atmosphere. With the elevators eliminated, the principal mechanical problems in moving beds result from the moving solids. Moving-bed vessels contain a large number of internal devices for injecting and withdrawing solids and gases. These devices must be fixed in place solidly enough to withstand the movement of the solids; yet they must permit thermal expansion and contraction on start-ups and shutdowns. The design of vessel internals has gradually improved as experience has been gained.

Moving beds also pose serious attrition problems, particularly in the various conveyers (elevators, gas lifts, mass lifts). Because the solids are usually expensive, careful consideration must be given to this aspect of the design (3,44). Experience has shown that attrition is less in smaller-diameter lift lines. Consequently, multiple lift lines are often used to hold diameters below about 12 in. (30). Typical flow rates through lift lines are 60 to 110 tons/hr/sq ft of cross section.

If the solids are adsorptive, they may require predrying before being charged to a moving-bed unit to avoid breakage from sudden expansion of their water contents (44).

FLUIDIZED BEDS

Fluidized beds differ from moving beds in that very fine powders are used, and the individual particles are in random motion, just as are the molecules of a liquid. Indeed, fluidized solids look like boiling liquids, and they have many of the properties of liquids. Attempts to utilize fluidized beds in the gasification of coal were made in the early 1920s, but their full possibilities were not recognized until they were tested for catalytic cracking twenty years later. Although fluidized beds have been used extensively since 1940, their basic principles are still not well understood.

Fluidized-bed Analogy

The fluidization of solids may be illustrated by means of an analogy (16). In Fig. 5-15, the effect of an upwardly flowing gas on a bed of solid particles is compared to the effect of temperature on a substance under its own vapor pressure. At low gas velocities, the bed is static and corresponds to the solid state of the substance at low temperatures. When the gas velocity reaches a critical value for the system, the bed particles begin to separate and to be supported by the gas; this point is comparable to the melting point of the solid. Over a limited range of gas velocities, the bed comprises a continuous dense phase that resembles a boiling liquid. As gas velocity increases over this range, increasing numbers of particles are carried above the surface by entrainment to constitute a dilute phase comparable to the vapor state. The density of the dilute phase progressively increases with gas velocity, while that of the dense phase decreases. The two phases thus coexist in the same way as the liquid and vapor states of a boiling liquid. At a second critical gas velocity, the two phases merge; this gas velocity is comparable to the critical temperature of a substance, above which only a single phase is possible. Continuing expansion with increasing fluid velocity is comparable to the expansion of a vapor at constant pressure with increasing temperature.

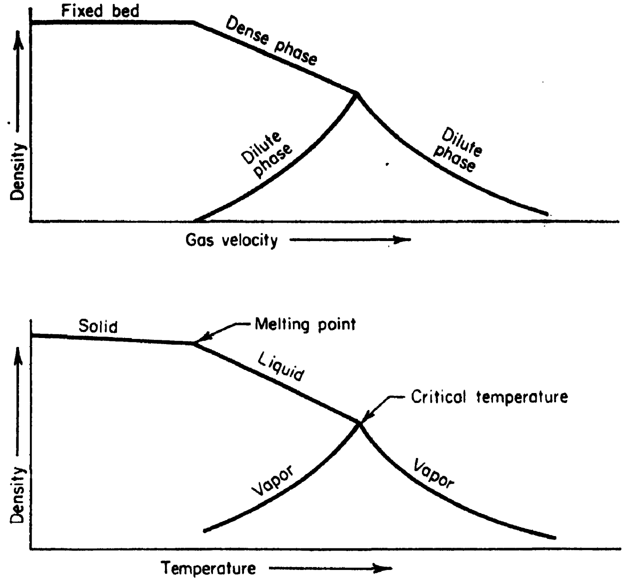

FIG. 5-15. Fluidized-solids analogy (16).

Although the foregoing analogy presents a good qualitative picture of fluidization, the critical velocities of the system are much less sharply defined than the boiling point and the critical temperature of a substance.

Properties of Fluidized Beds

Solids can be fluidized in any fluid—liquid or gas. Except for the pipelining of solids as water slurries (5) and the "finishing" of lubricating oils, fluidization with liquids has been of little interest, thus far, outside the laboratory (25). With gases, fluidization behavior depends principally on the size and density of the solid material and the linear velocity of the gas, although large differences in gas densities and viscosities also have some effect (15,26).

Catalyst Sizes and Gas Velocities. With clay-type cracking catalysts, the preferred size range is 20 to 80 μ in diameter, and superficial vapor velocities* are usually in the range of 1.5 to 4 ft per sec. In late-model units, design velocities are 2.5 ft per sec or higher (21).

Table 5-2. Typical Particle-size Distributions in Fluidization Processes (6)
(distributions in weight per cent)

Size, μ	Catalytic crackers[a]		Fluid hydroformers
	Electrostatic precipitators	Two stages of cyclones	
0–20	15–35	0	0–2
20–40	25–40	5–15	5–15
40–80	20–50	50–70	40–60
80+	5–15	20–40	30–50

Size, U.S. sieve	Fluid coking	Shale retorting	Coal carbonization	Phthalic anhydride manufacture
+8	1–4	2–5	0–10	0–8
−8, +20		65–85		
−20, +40	14–30		22–55	20–45
−40, +60	30–46		20–50	
−60, +80	20–45			
−80, +100				15–25
−100, +200	0–10		8–25	
−200	....	10–30	0–10	15–72

[a] Catalytic crackers usually lose catalyst only from the regenerator; the fines carried overhead from the reactor are scrubbed out of the gases and returned. All units have cyclones in the regenerator, and some have electrostatic precipitators to recover catalyst from the flue gas.

The size distribution in a fluidized bed at equilibrium depends upon the size distribution of the fresh solids and the rate at which they are added, the rate of attrition, the rate of loss, and the size distribution of the material lost. Size distributions for some typical operating units are given in Table 5-2.

Nonhomogeneity of Fluidized Beds. Except at very low velocities—far below the commercial range—fluidized beds are not homogeneous. Instead, most of the vapor rises as "bubbles" through a bed of solids

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* Superficial vapor velocities are calculated on the basis of empty vessels.

aerated by a small fraction of the vapor (6,26). Solids seem to "rain" through the bubbles, and the bubbles tend to coalesce as they rise (26). The density of the aerated-solids phase (exclusive of bubbles) appears to be about the same as the density of the unaerated solid when it is packed in the "loosest stable form" (10).

Flow Patterns of Solids. The particles of a fluidized bed are in violent motion. Attempts have been made to measure the mixing rate (1,12), but mixing was so rapid that little quantitative information was obtained. In a commercial unit, a small amount of a radioactively tagged catalyst was added to hundreds of tons of catalyst circulating between two vessels, and it was completely mixed with the circulating catalyst in less than an hour (20). The pattern of circulation is uncertain, although it is known that the solids tend to flow down near the walls of a vessel and up near the center (12,13), and there is some lateral motion also (22).

In view of the high circulation rates in a fluidized bed, it is surprising to find that the composition of the solids may vary through the bed. In beds having a high percentage of coarse particles, the coarse particles tend to concentrate toward the bottom of the bed (6). In units of recent design, fluidized beds with 5 to 6 min holding time in regenerators (where carbon is burned off a catalyst) were found to have zones of different carbon on catalyst, although older units, with greater holding times, did not show such variations.

Flow Patterns of Gases. The gas-flow pattern is also uncertain. It is definite that it is not piston flow; some back mixing of the gas occurs, the gas being carried down by downward-flowing catalyst, especially at the walls of the vessel (13). In comparison with a completely mixed bed, the amount of back mixing is small, even though residence-time experiments* with helium tracers gave results approximately those of a completely mixed bed (13). Bypassing of vapors is believed to account for this phenomenon (14). Bypassing is reduced by increasing the length-diameter ratio of the fluidized bed (13), but the reduction would be small in most commercial reactors unless vertical baffles were used.

When a second gas is introduced into an already fluidized bed, it is not distributed uniformly in the primary gas. Primary gas that passes up as bubbles moves past the injection point faster than does gas in the voids of the aerated bed. Thus, the bubbles receive proportionately less of the injected gas. In small-scale experiments, concentrations in the bubbles were only 20 to 65 per cent of the concentrations in the voids of the aerated bed (13).

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* A 10 per cent mixture of helium in air was passed through a fluidized bed. Then the helium was suddenly shut off, and its rate of exhaustion from the bed was determined.

Transfer of Solids

The principal advantage of fluidized solids lies in their mobility, which permits the ready transfer of solids to or from a reaction vessel without interrupting operations. Because the density of the fluidized mass can be changed by changing the gas velocity, a hydrostatic head can be used in place of pumps to effect such a transfer, as illustrated schematically in Fig. 5-16. The dense phase in the left leg of the U-tube creates a greater hydrostatic head than the dilute phase in the right leg, where the gas velocity is higher. Consequently, the dense-phase leg functions as a standpipe, and there is continuous flow from the left vessel to the right, although there may be no pressure differential between them. In practice, the rate of flow is often controlled by a slide valve at the base of the left leg, or standpipe. From the slide valve, the catalyst passes into a "riser" line, where it is picked up by a high-velocity gas stream and is carried into the next vessel.

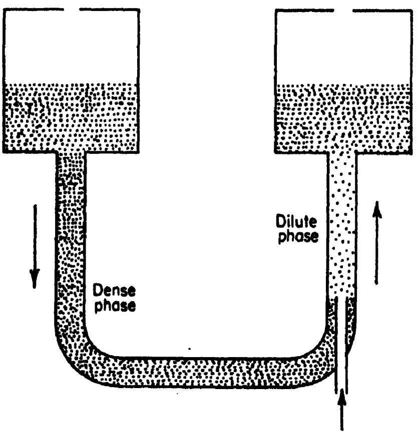

FIG. 5-16. Transfer of fluidized solids (16).

Standpipes. As fluidized solids enter a standpipe, they carry gas with them. Because the entrapped gas falls at a slower rate than the solids, the solid phase tends to lose gas and to defluidize. Also, the entrapped gas is compressed as it passes downward because of the head of fluidized solids in the standpipe. To counteract these effects, "aeration gas" is often injected at several points along the standpipe.

Flow difficulties have sometimes been experienced in standpipes, particularly in nonvertical sections. Whether the solids flow satisfactorily depends on the fluidity of the solids as well as on the design of the unit; the fluidity depends upon particle density, average size, and size distribution (9,26,48*b*) and also on particle shape. Fluidity improves as the density of the solids or as the average size of the particles is reduced, and a broader range of particle sizes gives better results than a mixture of closely sized fine and closely sized coarse particles. Increasing the concentration of fines (while keeping the average size constant) also improves fluidity, and circulation difficulties are often alleviated by the addition of a relatively small amount of fines. Presumably, the fines coat the coarser particles and prevent them from interlocking (48*b*). Beyond a definite concentration for each coarse material, the addition of more fines has little effect on fluidity.* Fluidity can be determined qualitatively from the rate at which solids deaerate (9). Certain materials—some oil shales, for example—have preferred fracture planes such that thin, flat particles are likely. Such particles fluidize much less readily than do the more usual materials (6).

The first few fluidized-bed systems employed an "upflow" design, in which the circulating solids passed overhead from each major vessel to separate cyclone systems from which they were recycled. How this design compares with a present "bottom-withdrawal" design is shown in Fig. 5-17.

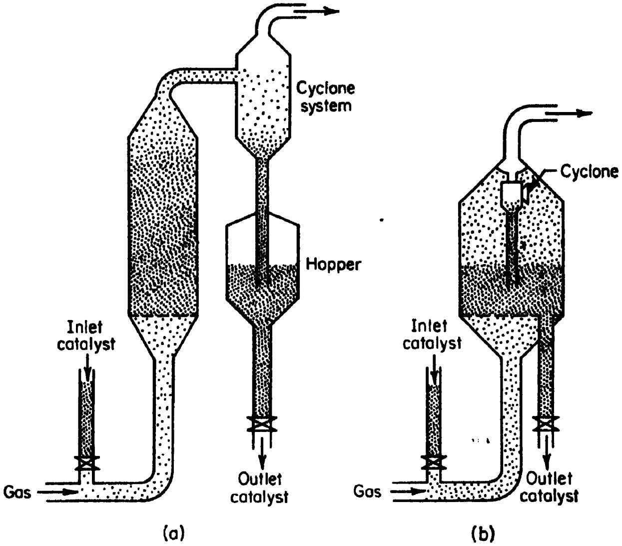

FIG. 5-17. Original and modern methods of circulating fluid catalysts (16). (*a*) Upflow. (*b*) Bottom withdrawal.

Risers. When a solid material is carried upward in a "riser" line by a high-velocity gas stream, it moves more slowly than the gas and more slowly than would be predicted by Stokes' law.† Two factors are involved—the "slip" of the solid particles in the gas stream (6,15) and the energy required to accelerate them to their ultimate velocity (6). Qualitatively, bends in transfer lines increase the slip factor,§ but the

* Theoretically, circulation difficulties could result from too high a concentration of fines (26). At an average particle size of 25 μ, clay-type catalysts have poor fluidization properties. At 10 μ, the catalyst forms agglomerates several millimeters in diameter. However, in commercial operations, the problem of too high a concentration of fines is seldom encountered, although it has been experienced in a unit designed for complete retention of all solids charged (21).

† Stokes' law defines the "free-fall" velocity of a single particle.

§ Slip factor is defined as the actual solids concentration in a riser divided by the concentration that would be achieved if the gas and solids moved at the same velocity.

quantitative relationship is not known. In the design of fluid catalytic crackers, slip factors of 2 have been used for dilute-phase riser lines with superficial gas velocities of 25 to 35 ft per sec.

Stripping of Solids. Frequently, the gases entrapped in fluidized solids are too valuable to be lost, and a "stripper" is provided to recover them. A stripper is merely a vessel (or a compartment in a vessel) through which the solids pass countercurrent to a rising "stripping gas"; stripped solids are withdrawn from the bottom. Because a fluidized bed approaches a thoroughly mixed vessel, poor stripping would be obtained in an unbaffled stripper. To improve stripping, various internals have been proposed (46) to increase the number of stripping stages. Among the most popular internals are vertical baffles that divide the stripper into compartments with large height-to-diameter ratios, and thus increase the number of countercurrent stages (13). Some examples are shown in Fig. 5-18. With such designs as these, stripping gas must be introduced to each compartment to avoid unbalanced operation, with stripping gas and solids flowing preferentially in different compartments. Inclined side-to-side baffles have also been used.

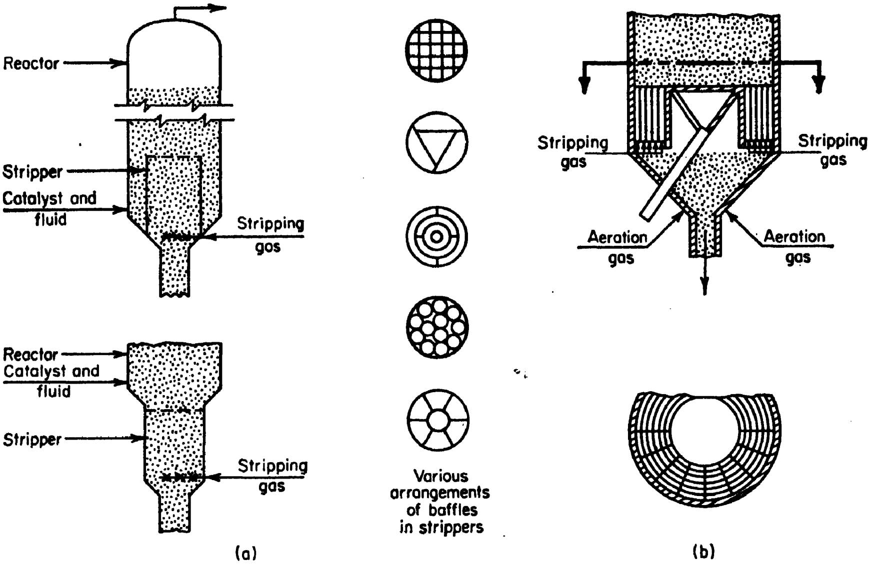

FIG. 5-18. Strippers for fluidized solids. (*a*) Internal and external cylindrical strippers. (*b*) Annular strippers.

Control of Solids Flow. For controlling the rate of solids flow, two schemes are used: controlled aeration and slide valves. Controlled aeration is the simpler system. With reference to Fig. 5-16, the rate of transfer from the left vessel to the right one can be controlled by controlling the rate of gas flow in the right leg of the U-tube. The greater the air supply, the lower is the density in the right leg and the greater the driving force for the flow of solids When this scheme is used, the lower portion of the U-tube is made in the form of a smooth curve.

Slide valves, illustrated in Fig. 5-19, provide more positive flow control, but their use increases the cost of the unit. The major part of the additional cost results from the pressure drops through the slide valves, which necessitate taller standpipes. Raising the reaction vessels (to provide taller standpipes) is costly.

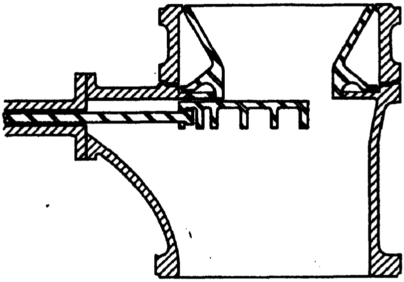

FIG. 5-19. Slide valve.

Recovery of Fines

Entrainment of solids from a fluidized bed increases with gas velocity and with gas density (15). Recovery of the entrained solids is required because the solids are usually expensive, because they otherwise would pollute the atmosphere, and because a considerable concentration of fines, which are preferentially entrained, is required in the circulating solids for satisfactory fluidization. For the primary separation, one to three stages of cyclone separators (33) are usually used, with inlet velocities of 60 to 70 ft per sec (28). These cyclones retain substantially all of the material larger than 20 μ. If further recovery is desired, electrical precipitators (33) are usually employed. Liquid scrubbers are also used to recover entrained fines, and micrometallic or ceramic filters (17,31) have been used in a few installations.

Retention of fines in a fluidized bed should reduce attrition by virtue of reducing the amount of larger material in the circulating solids. Also, it has been said that the presence of fines reduces the rate of attrition by cushioning the impacts between larger particles. However, the over-all effect of fines on losses is small except when the system is designed to retain particles in the range of 5 to 10 μ (6).

Temperature Control

Continuous mixing in the fluidized bed results in rapid transfer of heat throughout the bed. Even when endothermic or exothermic reactions occur in deep beds, no appreciable temperature differences are found. Surprisingly, this generalization holds even when the composition of the bed is not uniform (6). Effective thermal conductivities in a fluidized bed are as great as one hundred times that of silver (15).

Fluidized solids are efficient heat-transfer media. Consequently, they are especially suitable for a process in which temperature must be closely controlled despite a high heat of reaction, whether positive or negative. A large reactor of simple construction can be used, heat being supplied or removed by immersed coils or by circulation of the solids through an external heat exchanger. In commercial units, over-all heat-transfer coefficients range between 40 and 125 Btu/(hr)(sq ft)(°F) (15,16). Heat-transfer coefficients have been correlated for fluidized beds (27) and also for dilute-phase operations (11).

Vessel Design

The most difficult problem in the design of fluidized beds is to determine how much holdup of solids (usually catalysts) is required, and pilot-plant experimentation and commercial experience are usually used as a guide. If such information is not available, it is usually (but not always) conservative to assume a single reaction stage, that is, that the gas is in a completely mixed bed (13,14). From the standpoint of gaseous reactions, a high length-to-diameter ratio reduces solids-holdup requirements (14), but it is hard to obtain in a commercial unit. For the specialized application of adsorption, staged fluidized-solids systems have been proposed, as discussed in Chap. 4; they are similar to plate-type absorption columns, with powdered solids substituted for lean oil.

If the flow pattern of solids is an important consideration, design is difficult even if pilot-plant data are available (6). This situation might apply, for example, in the retorting of oil shale.

As with moving beds, the lowest cost for a given volume of a fluidized bed results from the use of the smallest practicable diameter. The gas rate usually determines the vessel diameter. Vessel height is determined by the inventory of solids and the height required to accommodate the cyclones or filter elements. These are put inside the vessel to avoid problems of thermal expansion. Putting cyclones inside the vessels also obviates the problem of designing them to withstand relatively large pressure differentials. Designing a cyclone to hold an internal pressure poses difficult problems, particularly in joining the narrow rectangular inlet tangentially to the cylindrical body of the cyclone. When cyclones are used, standpipes, or "diplegs," must be supplied to return the recovered fines to the fluidized beds. The diplegs of the first set of cyclones—the "primary cyclones"—are usually extended into the fluidized bed. Because a pressure loss is sustained in the cyclones, they operate at a lower pressure than does the fluidized bed. To return the recovered fines to the bed requires a dipleg height sufficient to overcome the pressure loss. Normally, this height sets the vapor space required above the bed. Material recovered in "secondary" and "tertiary" cyclones is finer than the material recovered in the primary cyclones. Consequently, the density of the solids phase in the diplegs is lower and a greater height would be required to return these fines directly to the bed. To avoid the additional height, secondary and tertiary diplegs are frequently terminated in the vapor space. Sealing devices are usually provided to prevent gas from passing up such diplegs, as illustrated in Fig. 5-20. Sealing devices are sometimes used on primary diplegs also.

To provide for good distribution of gas to a bed of fluidized solids, the bed is usually supported on a perforated grid, through which the gas passes. Design pressure drop through the grid is in the range of 1 to 2 psi (36). For mechanical reasons, grids are sometimes concave downward, which makes the bed slightly deeper at the center than near the walls of the vessel.

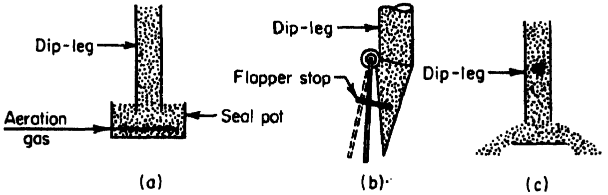

FIG. 5-20. Sealing devices for diplegs. (*a*) Seal pot. (*b*) Trickle valve. (*c*) Splash plate.

Design factors used for fluidized-bed catalytic-cracking units are shown in Table 5-3.

Table 5-3. Typical Design Factors for Fluidized-bed Catalytic Cracking Units (6,15,21)

Catalyst	20–80-μ clay-type materials
Superficial gas velocities, ft per sec:	
Reactors	1.5–4
Regenerators	1.5–4
Fluidized densities, lb per cu ft:	
Reactors and regenerators	20–35
Strippers	30–40
Standpipes	35–45
Risers	5–30
Diplegs	15–35
Velocities of solids, ft per sec:	
Standpipes	5
Risers	20–30, or higher
Diplegs	<5

Vessel Arrangements

Like moving-bed systems, fluidized-bed units have been built with the major vessels side by side or in a single structure (35). A side-by-side unit that employs slide valves to control catalyst flow is shown in Fig. 5-21. A similar unit employing aerated U-bends is illustrated in Fig. 5-22. In Fig. 5-23, a design is shown in which the reactor is "stacked" above the regenerator, and internal standpipes and risers are used.* Stacked designs are also used, in which the standpipes and risers are external to the vessels (38). All four types are employed in catalytic cracking of petroleum oils. When internal standpipes are used, plug valves are employed to control the flow of solids, because they are easier to install in internal standpipes than are slide valves. Conventional plug valves are modified to admit air or gas to the valve body inboard of the packing chamber to prevent solids from entering it (17).

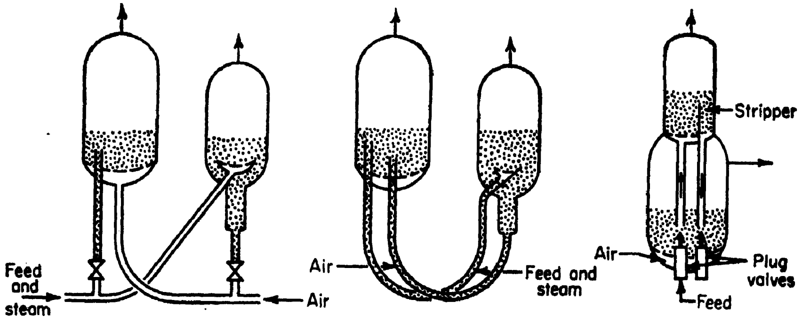

FIG. 5-21 FIG. 5-22 FIG. 5-23

FIGS. 5-21, 5-22, AND 5-23. Vessel arrangement for fluidized-bed systems.

Mechanical Problems

The major mechanical problem in fluidized-bed units is erosion, particularly at points of high velocity and where high-velocity solids-containing gas streams change directions (8,40). Erosion is most severe at a gas-impingement angle of 20 to 30° (6). Initially, erosion of slide valves was a major problem, and many units have been built with two in series. As experience has been gained, the designs of slide valves have improved, and their erosion has been greatly reduced (8,21,34,40*d*). Vessel linings are frequently used to reduce shell temperatures, and their erosion has also been a problem, particularly at the interfaces of fluidized beds. The use of mesh-reinforced linings, together with vapor stops to prevent channeling of gases behind the linings, has solved this problem (8). (Vapor stops are metal strips attached to the shell and projecting into the lining in such a way that any gas that penetrates the lining must follow a tortuous path.) Large catalyst-carrying lines may also be lined (40*b*). Erosion of regenerator stacks has caused some difficulties, erosion resulting from deflection of outgoing gases in passing through pressure-control valves. This problem has been solved by use of double-ported valves that keep the flue gas centered (40*b*). To minimize wear on stack valves, orifice plates are often used in series with them, the orifice plates taking a good share of the pressure drop.

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* This design, developed by M. W. Kellogg Co., is called "Orthoflow."

In passing through control valves and orifices, stack gases have sometimes created a noise problem, and silencers are often used to mitigate the problem.

Cyclone failures have also caused some operating difficulties. In addition to the obvious problem of high losses of solids, cyclone failures may cause solids-circulation difficulties, resulting from the preferential loss of fines from the circulating solids. Multiclones are more efficient than cyclones, but they are not often used because they are more subject to erosion (6). Ceramic liners are frequently used in cyclones to reduce erosive wear.

To provide for thermal expansion, flexible piping joints are often needed. Bellows-type expansion joints with internal sleeves are used (8).

When large curved risers are employed, the risers may move as much as 3 or 4 in. in a slow, periodic motion (6). Presumably, this movement results from the accumulation of solids on the "far side" of the bend, which are blown off periodically by pressure surges. Such lines must be tied down in a manner that will prevent damage from vibrations, but will still permit thermal expansion.

When solids-circulation difficulties are encountered, they may be corrected by withdrawing a part of the solids and replacing it with solids of the desired size range, by elutriating the solids and discarding the unwanted portion, or by the use of an attrition device (6).

In most cases, the introduction of solids into a reactor is no problem; they are simply introduced via a typical riser line. With some materials—including sulfide minerals, dry pyrites, and calcium carbonate—special feeding arrangements are required (43).

MOVING BEDS VERSUS FLUIDIZED BEDS

Moving beds and fluidized beds are natural rivals. Inasmuch as both have been used extensively for the catalytic cracking of petroleum oils, there are differences of opinion as to their relative merits. However, each has definite advantages in certain respects, and thus for particular applications. Moving beds have the edge where staging is important. Fluidized beds have advantages where close temperature control is desired for an endothermic or an exothermic reaction, or where high solids-circulation rates are desired. Fluidized beds can be built in larger sizes, and this is a substantial advantage in many cases.

Staging

Staging is important for high-conversion systems. When conversions are only about 50 per cent, staging is of secondary importance (3,13). Even at 70 per cent, its importance is not large. At conversion levels in the range of 98 per cent, however, staging is a major design factor. Such operations might be desulfurization of petroleum stocks or adsorption of ethylene from gases (2). For such operations, moving beds appear to have the advantage, although, as discussed in Chap. 4, staging of fluidized solids has been proved in pilot-plant adsorption operations.

Temperature Control

When isothermal operation is desired for a highly endothermic or exothermic reaction, fluidized beds have two large advantages over moving beds. First of all, temperatures are substantially constant in all fluidized beds. Even when reactions with large heat effects are carried out in large fluidized beds, the temperature variations are only a few degrees. Second, fluidized beds have heat-transfer coefficients several times greater than moving beds have. Consequently, heat can be supplied to the fluidized solids, or removed from them, much more readily.

The temperature gradient in a moving bed is adiabatic. Wherever an adiabatic gradient is desired, moving beds would have an advantage.

Solids-circulation Rates

In some applications, high solids-circulation rates are advantageous. In catalytic cracking, for example, high rates permit the transfer of regeneration heat (from the burning of coke) to the reactor, where it can be used to vaporize the feed stock and heat it to reaction temperatures. Thus, all-liquid feeds can be charged to fluid-catalytic-cracking units, whereas moving-bed units usually operate with the feed only about 25 per cent liquid (45), although as much as 90 per cent liquid has been charged (18).

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CHAPTER 6

PYROLYSIS

Almost from the beginning of the petroleum industry, it was known that high-boiling oils could be converted into lower-boiling materials such as gasoline by heating to high temperatures. A patent on such a process was granted as early as 1865, and miniature commercial units were in operation in 1886, and possibly earlier (14). The possibilities of the process challenged many investigators, and several larger-scale commercial ventures were tried, but none proved successful until the Burton process was commercialized in 1913.* The success of this process revolutionized the industry. Further, by demonstrating the value of applied scientific principles, the Burton process precipitated a general application of science to petroleum refining (88). Indeed, its effects are still apparent in the rapidly changing technology of today.

Although the original purpose of pyrolysis was—and, for the most part, still is—the cracking of larger molecules into smaller ones, some higher-boiling materials are also produced. In some applications, the production of higher-boiling materials has been deliberately fostered. Thus, pyrolysis is now defined as the treatment of hydrocarbons at high temperatures to change their molecular weights—either downward or upward.

REACTION PATTERNS

Although feed stocks to pyrolysis range from ethane to crude-oil residues, the reaction patterns for most of them are similar. To illustrate this point, reaction patterns for two feed stocks—propane and gas oil—are discussed in the following paragraphs.

Propane Cracking. Figure 6-1 illustrates the pyrolysis of propane to produce ethylene. Cracking and dehydrogenation are the primary reactions (70):

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* The Burton process was developed by the Standard Oil Co. (Indiana). Later processes include Holmes-Manley (Texas Company), Dubbs (Universal Oil Products Co.), Isom (Sinclair Oil Co.), Fleming (Shell Oil Company), Cross (Gasoline Products Co.), and Tube-and-Tank [Standard Oil Co. (New Jersey)].

$$CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_2$$
$$2CH_3CH_2CH_3 \rightarrow 2CH_3CH_3 + CH_2CH_2$$
$$CH_3CH_2CH_3 \rightarrow CH_3CHCH_2 + H_2$$

The primary products may react further in a variety of ways. These include cracking of propene to produce more ethylene, polymerization of ethylene and other olefins to form larger molecules, cyclization of polymers to naphthenes, dehydrogenation of naphthenes to aromatics, and condensation of aromatics to form larger molecules and eventually coke. Ethylene itself continues to polymerize. Over-all, the reactions may be summarized as follows:

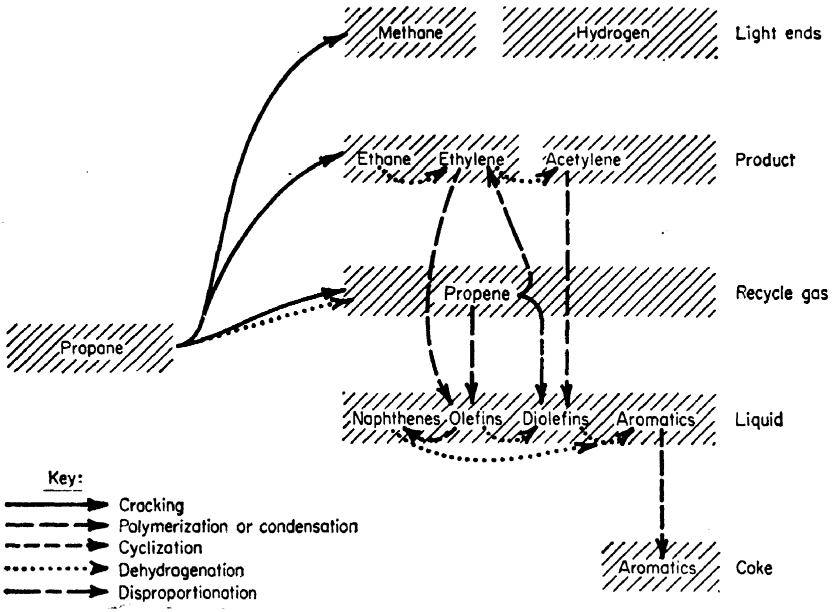

FIG. 6-1. Probable reactions in thermal cracking of propane.

1. Cracking of propane to produce ethylene, propene, and light ends.
2. Cracking of ethylene (relatively slow).
3. Reaction of ethylene and propene to produce larger molecules, including aromatic liquids and eventually coke.
4. Cracking of propene and heavier materials to produce ethylene and light ends.

Because the light ends and the aromatics are the most stable products, their concentrations increase faster than those of the other materials, including ethylene. Hence, the higher the conversion, the lower is the percentage of converted propane that appears as ethylene. Also, the higher the conversion, the larger become the condensed aromatics and the greater is the tendency toward coke production. For both these reasons, conversion is not carried to completion in a single pass. Rather, it is interrupted at an intermediate point, and the unconverted material is separated from the product and is recycled. Of course, the lower the conversion per pass, the larger is the plant size for a given over-all conversion.

Gas-Oil Cracking. For the cracking of virgin gas oil, the reaction pattern is shown in Fig. 6-2. Paraffins crack to olefins and smaller paraffins in the gas, gasoline, and gas-oil boiling ranges. Side chains of alkyl naphthenes and alkyl aromatics crack to yield olefins plus naphthenes and aromatics with shorter side chains. Aromatics condense to larger molecules. All the primary products except the aromatics crack further as the reaction proceeds. Also, olefins polymerize to larger molecules and cyclize to naphthenes, including condensed-ring naphthenes. Naphthenes dehydrogenate to aromatics, and condensed-ring aromatics condense to larger molecules and eventually coke.* The over-all effects may be summarized as follows:

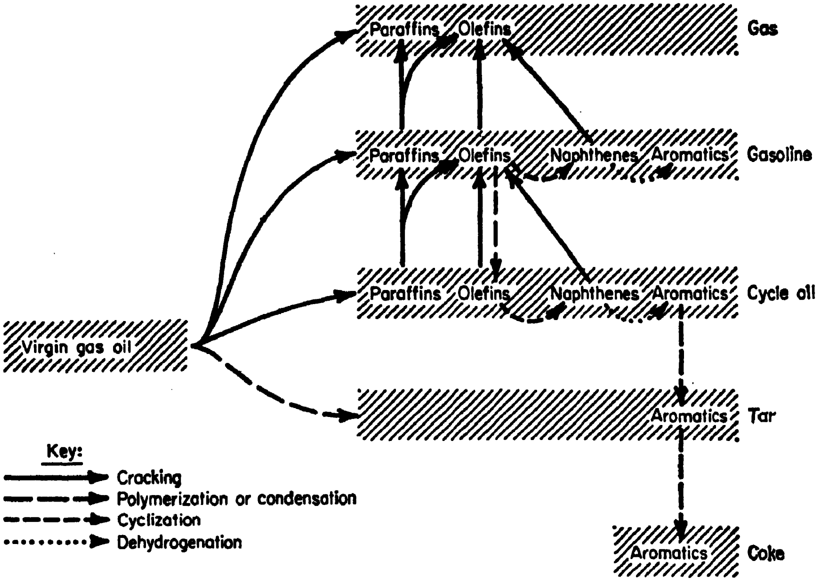

Fig. 6-2. Probable reactions in thermal cracking of virgin gas oil.

1. Cracking of paraffins, alkyl naphthenes, and alkyl aromatics to gas, gasoline, and cracked gas oil.
2. Cracking of gasoline to gas.

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* It is presumed that coke results from the condensation of aromatics. However, the patent literature (51) and the trade literature (34) suggest that paraffins may be the chief coke formers.

3. Reaction of olefins to produce larger molecules, including aromatic heavy ends ("tar") and eventually coke.
4. Further cracking of cracked gas oil to produce gasoline and gas.

These effects are exactly analogous to those enumerated for the cracking of propane. The effects of increasing conversion per pass are also analogous—lower yield of gasoline per unit of gas oil converted and an increased tendency toward the production of coke. Accordingly, relatively low conversions per pass are employed, and the unconverted material is separated by distillation and recycled with the cracked gas oil as "cycle oil."

REACTION MECHANISM

A number of theories have been advanced to explain pyrolytic reactions, but none of them explains all the experimental results (25). The most popular mechanism involves free radicals, that is, electrically neutral, but highly reactive particles formed by the rupture of C—C or C—H bonds, with each fragment retaining one of the pair of shared electrons that made up the bond. When hydrocarbons are heated to high temperatures, some fraction of them dissociates into free radicals. Typically,

$$\begin{aligned} CH_4 &\rightarrow H\cdot + CH_3\cdot \\ C_2H_6 &\rightarrow H\cdot + C_2H_5\cdot \text{ or } CH_3\cdot + CH_3\cdot \\ C_3H_8 &\rightarrow H\cdot + C_3H_7\cdot \text{ or } CH_3\cdot + C_2H_5\cdot \\ C_4H_{10} &\rightarrow H\cdot + C_4H_9\cdot \text{ or } CH_3\cdot + C_3H_7\cdot \\ &\qquad \text{or } C_2H_5\cdot + C_2H_5\cdot \end{aligned}$$

Hydrogen, methyl, and ethyl radicals are relatively stable, whereas the larger radicals break down immediately. For example,

$$\begin{aligned} C_3H_7\cdot &\rightarrow C_3H_6 + H\cdot \text{ or } C_2H_4 + CH_3\cdot \\ C_4H_9\cdot &\rightarrow C_4H_8 + H\cdot \text{ or } C_3H_6 + CH_3\cdot \text{ or } C_2H_4 + C_2H_5\cdot \end{aligned}$$

From each larger radical, then, an olefin and a smaller, more stable radical are obtained.

The "stable" radicals react with hydrocarbons by extracting hydrogen atoms, and thus forming new radicals:

$$CH_3\cdot + RH \rightarrow CH_4 + R\cdot$$

If R is a large alkyl group, it breaks down immediately into an olefin and a smaller radical, which reacts further. Thus, a chain reaction is instituted, which is terminated only when a radical reacts with another radical or with an extraneous material, such as a reactor surface. Alkyl chains on naphthenic or aromatic rings are presumed to react in the same way as do paraffins.

Simple mathematical relationships based on the free-radical theory predict very closely the experimental yields in the pyrolysis of propane, butanes, pentanes, and hexanes (68). For heavier stocks, such as gas oils, the feeds are too complex for mathematical treatment.

The free-radical theory explains cracking reactions, but it does not account for the production of materials heavier than the feed. These are presumed to result from polymerization of olefins and condensation of aromatics, although alkylation may also occur. In any case, pyrolysis always converts part of the feed into heavier, as well as lighter, products. Inasmuch as higher pressures promote the molecule-building reactions, high pressures are used when these reactions are desired, lower pressures when they are not.

At moderately high temperatures—1400 to 1600°F—substantial amounts of butadiene and aromatics are formed (24), probably by free-radical decompositions of olefins and cyclohexanes. Aromatics are presumed to result from the reaction of butadiene with olefins to produce cyclic olefins, which dehydrogenate to aromatics. Because lower pressures slow the rate at which butadiene reacts (16), low pressures are used when butadiene is the desired product.

REACTION CONDITIONS

Three factors determine the reaction conditions for any given operation: the products desired, the ease with which the feed reacts, and the tendency to form coke. Typical conditions are listed in Table 6-1.

Table 6-1. Typical Reaction Conditions for Thermal Processes

Feed	Operation	Time, sec	Final reaction conditions	
			Temp., °F	Pressure, psig
Methane	Acetylene production	<0.1	2500	<0
Methane	Production of carbon black	.....	2500	0
Ethane	Ethylene production	1	1500	15
Propane	Ethylene production	1	1430	15
Butane	Thermal polymerization	60	1050	2,000
Propane, naphtha	Gas reversion	.....	1050	1,500
Naphtha	Thermal reforming	300	1000	700
Gas oil	Thermal cracking	60	925	300
Reduced crude	Coking	.....	900	10–40
Reduced crude	Visbreaking	.....	900	250

Product Stabilities. The various products from cracking differ in their stabilities to heat. Thus the predominant products change with temperature. Favorable temperature ranges are given in Table 6-2.

Table 6-2

Product	*Temperature, °F*
Gasoline	850–1000
Ethylene	1100–1500
Acetylene	2000+
Carbon black	2000+

Inasmuch as acetylene and carbon black are formed in the same temperature range, and because carbon black is the ultimate product, the production of acetylene requires careful control of reaction severity.

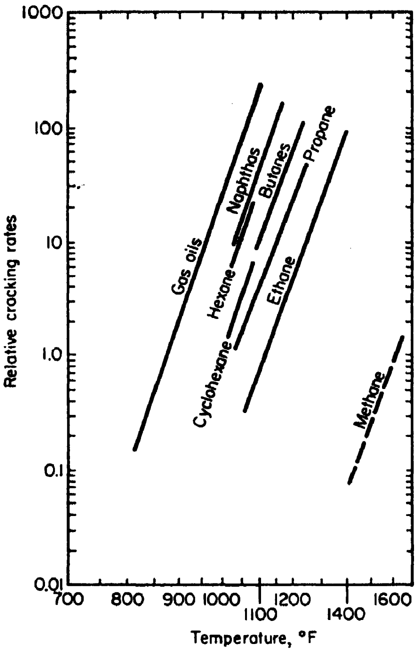

FIG. 6-3. Relative cracking rates of hydrocarbons.

Ease of Cracking. There are large differences in the responses of hydrocarbons to pyrolysis conditions, the highest-boiling compounds reacting most readily (44). As illustrated in Fig. 6-3, a gas oil reacts about 5 times as fast as a naphtha, about 50 times as fast as propane, about 300 times as fast as ethane, and about 400,000 times as fast as methane. Comparative conversions for several stocks are given in Fig. 6-4. From these rates, it is readily seen that high temperatures are required for satisfactory reaction rates with lower-molecular-weight materials.

Coking Tendency. Coking tendency increases with the molecular weight of the charge stock, presumably because the higher-molecular-weight materials do not have as far to go. Maximum practical severity of the pyrolysis treatment, as limited by coking tendency, has been related to the specific gravity of the reactor charge; the relationship is shown in Fig. 6-5. The coking limitation does not apply, of course, to a unit designed in such a way that coking does not interfere with operations.

Experiments have shown that coking results from condensation of certain aromatic free radicals and that it can be hindered by adding hydrogen donors (such as tetralin) to the feed (4,9). Condensation occurs more readily in the liquid phase, and anthracene structures are much more likely to condense than phenanthrene-type molecules (39*a*).

Effect of Pressure. Increasing the pressure increases the rates of the polymerization and condensation reactions. Whether or not it is desir-

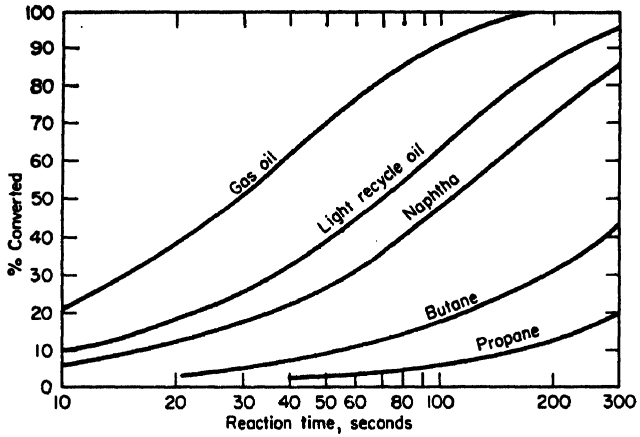

FIG. 6-4. Thermal conversions at 1020°F (49).

able to increase these rates depends upon the purpose of the operation. Increasing pressure may have the further effect of increasing the permissible throughput in a given unit.

Quenching. In most pyrolysis operations, reactor effluent is quenched to a temperature low enough to stop the reaction at the desired point or to avoid the formation of coke in the product-handling equipment. Quench temperatures are usually in the neighborhood of 700°F.

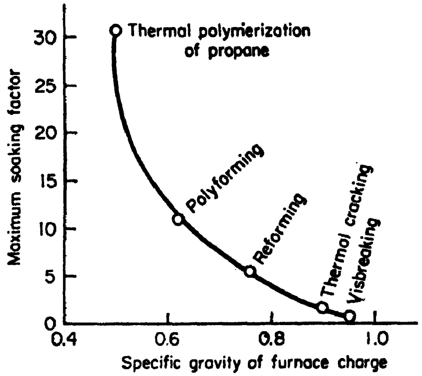

FIG. 6-5. Maximum cracking intensity in furnace-type units (82). Soaking factor is

$$F = \frac{C}{V}\int_0^1 \frac{P_T}{750}\frac{K_T}{K_{800}}\,dz$$

where C = coil volume above 800°F, V = daily throughput in barrels, K_T and K_{800} are reaction velocity contents, P_T is pressure, and Z is the fractional coil volume above 800°F.

OPERATIONS

The first pyrolysis units were built to make gasoline from other materials, and this has continued to be the principal objective. However, a considerable number have been built to make ethylene, to improve the octane ratings of virgin gasolines, to reduce the viscosities of heavy fuels, and for various other purposes. At the present time, the most important applications are production of ethylene, cracking of cycle oils from catalytic cracking, and coking of reduced crudes.

Ethylene Production

Ethylene is the basic raw material for a large number of chemicals, including alcohols, acids, ketones, halogenated hydrocarbons, and polyethylene. Although some is recovered from refinery gases, the bulk of it is produced by the cracking of refinery gases and of liquid hydrocarbons. At least one refiner is manufacturing ethylene on a large scale and distributing it by pipe line to customers (10).

The preferred charge stocks for cracking are refinery gases, although heavy naphthas and gas oils are sometimes used (55,65,80). When refinery gases are employed, ethylene is first removed from the gas stream and an ethane-propene-propane residue is charged to cracking. Reaction begins at about 1000°F and becomes appreciable at about 1150°F. In most present units, maximum temperatures range between 1400 and 1500°F, and reaction time above 1150°F is in the neighborhood of 1 to 2 sec. Higher yields of ethylene are obtained at lower pressures, because polymerization increases with pressure. However, lower pressures increase recovery costs by increasing compression requirements. Reactor outlet pressures of 5 to 30 psig are generally employed.

During operation, coke is laid down on the reactor surfaces. When the reaction is carried out in furnace tubes, only a thin layer of coke is permissible because it increases the already high tube-wall temperatures. When the coke film reaches a thickness of about $\frac{1}{16}$ in., the operation is interrupted and the coke is burned out by a mixture of steam and air. Coke deposition limits propane conversions in such units to about 85 per cent. If appreciable amounts of propene are present in the feed, the maximum propane conversion is about 75 per cent, and the corresponding propene and ethane conversions are 45 and 35 per cent.

Sometimes propene is separated from the feed and the reactor effluent, and only ethane and propane are charged to cracking. In such cases, separate reactors may be used for the two gases to permit using the conditions optimum for each (54).

Ultimate yields of ethylene when recycling to completion in a furnace-type reactor are as follows:

For ethane	0.8 mole ethylene per mole
For propane	0.5 mole ethylene per mole
For propene	0.4 mole ethylene per mole

Better yields are claimed for a moving-bed* type of unit (35,71).

Thermal Polymerization

Thermal polymerization was developed about 1930 to convert paraffinic and olefinic gases to gasoline. Because catalytic processes were devel-

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* Moving-beds are discussed in Chap. 5.

oped very shortly thereafter, thermal polymerization proved to be a very short-lived process. It cannot compete with the catalytic processes for the polymerization (or alkylation) of olefins, and the butanes available in a refinery can generally be blended into motor gasoline if the butenes are polymerized or alkylated.

Butane-rich streams are the usual charge stocks to thermal polymerization; lighter stocks are not charged because they require severe reaction conditions (46). Temperatures of 1000 to 1050°F and pressures of 1,000 to 2,000 psi are usual, and typical reaction times are 5 to 100 sec (21). If pressures as low as 60 psi are used in conjunction with high temperatures, the product is rich in aromatics, especially benzene and toluene.

Product yields have been correlated against reaction conditions (40). Gasoline yields increase with increasing pressure and with increasing recycle ratio (lower conversion per pass). Ultimate yields are in the range of 62 to 72 wt per cent gasoline and 5 to 10 per cent heavy tar. With 3 cc of tetraethyllead, the gasoline product has a research rating of 94 to 96 (86). Its clear rating is about 77. Thermally polymerized gasolines tend to form gum, but clay treating* makes them satisfactory in this respect.

Reforming

Pyrolysis of gasoline fractions is called "thermal reforming" or simply "reforming." Because most virgin gasolines are composed largely of paraffins and naphthenes, they have low octane numbers. Reforming converts paraffins to olefins and thus raises octane number. Reforming also shifts the boiling range of the product, making it more volatile, and this shift further increases the octane of the product. In the operation,

Table 6-3. Typical Thermal Reforming Yields (63)

	Feed	Products		
		Gas	Gasoline	Tar
Yields:				
Vol %	100	....	81.3	4.2
Wt %	100	15.3		
Octane ratings:				
Motor, clear	40.5	....	70.2	
Motor, with 3 cc TEL	.....	....	81.9	
Research, clear	.....	....	78.2	
Research, with 3 cc TEL	.....	....	91.3	
Reid vapor pressure, lb	1.5	....	10.0	
Gravity, °API	53.0	....	56.1	18.2

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* Clay treating is discussed in Chap. 13.

some gasoline is cracked to gas, and some is polymerized to tar. A typical yield pattern is shown in Table 6-3. Improvement in octane rating is related to the gasoline loss and is also a function of the original octane number, as shown in Table 6-4 (45). The octane-rating method for the above tests was not stated; it was probably the motor method. Research octane numbers of product gasolines (20,37) are as much as 10 units higher than these figures.

Table 6-4

Feed octane	Product octane vs per cent loss of gasoline					
	5%	10%	15%	20%	25%	40%
35	....	65	67	68	69	72.5
40	....	66.5	68	69.5	70.5	73.5
45	....	67	69	70	72	75
50	66	68.5	70	71.5	73	77
55	67.5	70	72	73	75	

Because extensive conversion of the gasoline is not desired, recycling is not practiced in reforming. Recycling the heavier portion of the gasoline (315 to 365°F) has been carried out experimentally (37). For a given octane improvement, losses were greater than in once-through operations.

Thermally cracked naphthas have also been reformed experimentally (37). Gasoline losses per unit of octane improvement were higher than for virgin naphthas; however, the octane of the fresh feed was much higher. If the virgin naphtha is first reformed to the octane quality of the thermal naphtha, further reforming gives the same yield-octane relationship.

"Reforming" of a mixture of catalytic heavy naphtha and light catalytic cycle oil (380 to 512°F) gave about 50 per cent yield of 98–99 research octane gasoline, clear (66). The operation may be applicable where the heaviest catalytic naphtha is of low octane quality because of the inclusion of virgin naphtha in the charge to catalytic cracking.

Thermal reforming has been almost completely replaced by catalytic processes, although there is some interest in the thermal reforming of products from catalytic reforming (61).*

Gas Reversion†

Gas reversion combines the thermal polymerization and reforming processes. Like thermal polymerization, gas reversion was almost imme-

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* Catalytic reforming is discussed in Chap. 8.

† Gas-reversion processes were developed by the Phillips Petroleum Co. and the Gulf Oil Corporation. One version is called "Polyforming."

diately outmoded by the development of catalytic polymerization and, later, of catalytic reforming. However, some gas-reversion units were still in operation in 1955, and operating correlations have been published (8,86).

In a gas-reversion unit, a mixture of propane, propene, butanes, butenes, and naphtha is charged to the pyrolysis reactor to polymerize the light gases and to reform the naphtha. Unconverted C_3's and C_4's are recycled. The operation is usually carried out at 1,000 to 1,500 psi and about 1050°F.

Thermal Cracking

The term "thermal cracking" is generally applied to the pyrolysis of distillates heavier than gasoline, although it is sometimes applied to other feed stocks also. Three types of thermal cracking processes have been employed: liquid-phase, vapor-phase, and mixed-phase. Gruse and Stevens (26) give the following arbitrary classification:

Liquid-phase: 750–850°F; 200+ psi
Mixed-phase: 850–1000°F; 200–1,500 psi
Vapor-phase: 1000–1150°F; 50–200 psi

Most present operations are mixed phase, operating pressures ranging from 200 to 1,000 psi, operating temperatures from 900 to 980°F.

From time to time, vapor-phase processes were attempted, but none proved very successful. These processes operated at low pressures, high temperatures, and short contact times; typically, 50 psi, 1100°F, and 5 sec. The principal advantage over liquid-phase or mixed-phase operation is a higher octane product, but it is achieved at the expense of gasoline yield. Coking of furnace tubes was the major problem in vapor-phase units (17).

Feed Stocks and Products. Until the advent of catalytic cracking, virgin gas oils were charged to thermal cracking. Thermal cracking facilities now process cycle oils from catalytic cracking principally. As in other pyrolytic processes, the feed stock is only partially converted in a single pass. The furnace effluent is quenched and the products are separated into gas, gasoline, thermal cycle stock, and tar. As shown in Fig. 6-6, yields (from a series of pilot-plant operations at about 500 psi) can be correlated against the specific gravity of the feed stock (41). The yields from catalytic cycle oils are poorer than the yields from virgin stocks, because the least-refractory material has already been converted in the catalytic operation.

The research octane numbers of most gasolines produced from virgin gas oils range between 65 and 75, clear (although gasolines from highly naphthenic gas oils may rate higher than 86 (45)). Octane number increases with increasing conversion/pass. Octane ratings of gasolines made from catalytic cycle oils are 1 to 2 units lower than of gasolines from virgin gas oils of the same specific gravity (41).

Methods for estimating thermal-cracking yields have been summarized by Nelson (43).

Operating Conditions. Little has been published on the thermal cracking of catalytic cycle oils in commercial equipment. It is probable, however, that catalytic stocks respond qualitatively to cracking conditions as do virgin stocks, for which the following generalizations hold:

1. Higher pressures favor condensation, and tar production increases.
2. Lower pressures favor the production of gas.
3. Over the range of commercial operating pressures (200 to 1,000 psi), the lower tar production obtained at lower pressures more than counterbalances the increased production of gas; thus a higher yield is obtained at lower pressures (81). However, the situation may reverse at higher pressures. Higher yields have been obtained at 1,500 psi than at 750 psi in pilot-scale cracking of catalytic cycle oils (38).

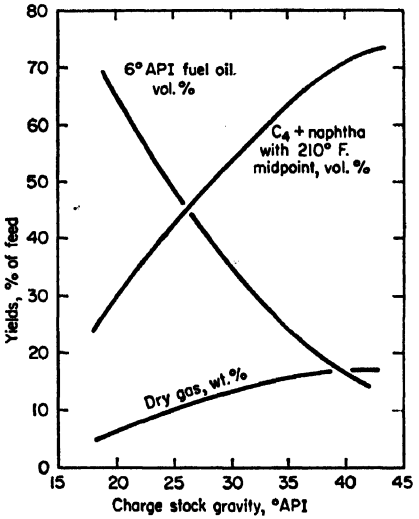

FIG. 6-6. Yields from thermal cracking of catalytic cycle oils (41).

4. The ultimate yield of gasoline goes down with increasing conversion per pass. This reduction results from secondary reactions of gasoline boiling-range materials.
5. Increasing conversion per pass increases coke production.

In the cracking of catalytic cycle oils, conversions (defined as per cent of gas oil disappearance per cycle) are in the neighborhood of 20 per cent. Run lengths are limited by coke formation in the reaction equipment, and typical run lengths are 40 days (52).

The principal effect of temperature is on reaction rate, the rate doubling for every increase of 25 to 30°F in the range of 950 to 1000°F (33). In a mixed-phase unit, this effect is partially counterbalanced by additional vaporization at the higher temperature, which increases the volume of the charge and thereby reduces the reaction time.

Visbreaking

When reduced crudes are pyrolyzed without substantial coke production, the process is called visbreaking. The process was developed to lower the viscosities and pour points of residual stocks and thus reduce the amounts of less-viscous (and more valuable) blending oils required to make the residual stocks salable as fuel oils. Gasoline and gas oil are produced, the amounts depending upon the intensity of the operation.

Because residual stocks have greater coking tendencies than gas oils, lower temperatures are employed in visbreaking than in thermal cracking. Typical reaction conditions are about 900°F and 250 psi, and recycle is not usually employed. If conditions are carefully controlled, very heavy residues can be visbroken; a stock containing 13 per cent Conradson carbon has been processed commercially (6). The patent literature (51) indicates that coking tendency is reduced if vacuum distillation is employed to produce a very heavy charge stock; reaction temperatures up to 1000°F are indicated.

Table 6-5. Visbreaking of Crude Residues

	Inspections and yields (2,6)	
Charge stock:		
Gravity, °API	20.3	11.2
Viscosity, SSF at 122°F	500	
Viscosity, SSF at 210°F	.....	99
Carbon residue, wt %	10.5	13.1
Sulfur, wt %	.....	3.23
Yields, vol %:		
Butanes, butenes	.....	2.0
Gasoline	7.0	9.8
Heating oil	.....	9.5
Gas oil	12.4	8.0
Fuel oil (300 SSF at 122°F)	80.4	70.7
Properties of gasoline:		
Research octane number, clear	60.0	73.2
Research octane number, 3 cc TEL	70.9	83.1
Reid vapor pressure, lb	3.5	7.6
Sulfur, wt %	.....	0.34
Properties of heating oil:		
Gravity, °API	.....	38.9
Sulfur, wt %	.....	1.39
Diesel index	.....	50.2
Properties of gas oil:		
Gravity, °API	35.5	24.1
Sulfur, wt %	.....	1.86
Diesel index	.....	41.9
Aniline point, °F	180	
Carbon residue, wt %	0.3	0.21

To minimize coking, rapid, even heating of the charge stock is desirable (2). High vapor velocities also minimize coking, and steam or water may be injected into the feed to increase them (2,6). More severe pyrolysis conditions can be employed when steam or water injection is used.

A precracked feed stock may promote coking. In one case, elimination of mild cracking in the vacuum unit that supplied feed to a visbreaker increased visbreaker run lengths from only 2 to 3 days to about 40 days (2).

Two visbreaking operations on heavy charge stocks are summarized in Table 6-5.

Coking

Coking is similar in principle to visbreaking except that more severe conditions are used and the reduced crude is completely converted to lighter and heavier materials. (The equipment required is rather different.) The light products (resulting from cracking) are gas, some gasoline, and gas oil. The heavy product (resulting from condensation reactions) is coke. Typical coking yields are (30):

Gas	5 wt %
Gasoline	20 vol %
Gas oil	60–70 vol %
Coke	10–15 wt %

Coking has an advantage over visbreaking in that it produces more distillates from a given charge. The yield of distillates, particularly gas oil, is maximized by coking at low pressures. At higher pressures, more gas and coke are produced, and the liquid product contains more gasoline (48,57).

The yields of gas and gasoline increase with increasing temperature; the yield of gas oil decreases. Also the research octane number of the gasoline increases linearly with temperature, for example, from 72 (clear) at 930°F to 87 at 1050°F (42). However, gasolines produced at higher temperatures are unstable and require finishing operations, such as clay treating or mild hydrogenation (84). The gases produced at higher temperatures are more olefinic. At an average reaction temperature of 955°F, they are 50 per cent olefinic, as compared with 15 per cent for temperatures of about 850°F.

In early lubricating-oil manufacturing operations, "coking distillation" was sometimes practiced "to reduce the viscosity of the wax distillate (in case it is too high), to decompose poorly crystalline higher-molecular-weight waxes into more crystalline materials and to destroy crystallization inhibitors . . . " prior to dewaxing (29). This operation has been abandoned.

Other Operations

Pyrolysis is often employed to make chemicals under conditions more severe than usual in petroleum refining. The production of ethylene, which has already been described, is more properly considered a chemicals operation. Other chemical products are aromatics, butadiene, acetylene, and carbon black.

The products from any pyrolysis operation depend principally on the temperature and the contact time. In the order of increasing stability to heat, reaction products line up as follows (18):

Olefins and naphthene polymers
Diolefins and triolefins
Benzene and toluene
Aromatic tars
Methane
Acetylene
Carbon

In most pyrolysis products, the first four groups predominate. Either ethylene or the total liquid constitutes the primary product from most plants, but some have been operated to produce a broad range of aromatics (7,65,78,80), and some, (during World War II) butadiene. Acetylene is produced at high temperatures (2000 to 5400°F), and extremely short reaction times are required to prevent its further decomposition into carbon (75). In some plants, longer contact times are used deliberately to produce carbon black (79) at temperatures of 2100 to 2800°F. For the production of acetylene or carbon black, any hydrocarbon can be used as charge stock, even methane.

PROCESS EQUIPMENT

Although some of the early attempts to develop cracking processes were based on continuous operations, the first commercial process was operated batchwise. Burton cracking units employed batch distillation of crude oils under sufficient pressure (75 to 95 psi) that materials higher boiling than gasoline remained liquid until cracking temperatures were reached—about 750°F—and cracked products passed off as vapor. The original stills were riveted vessels, 8 ft in diameter by 20 ft long, with seams caulked to prevent leakage of vapors. With a charging capacity of 200 to 250 bbl, they were operated on a 48-hr cycle. Heat was supplied through the shell of the still by direct firing. Later Burton units were semicontinuous.

Coking of reduced crudes at atmospheric pressure antedated thermal cracking of gas oils. Except that it operated at lower pressures, coking was carried out in the same kind of equipment as was used in thermal cracking (83). Coking units of this type (of all-welded construction) are still in operation. In addition to employing lower pressures, the operation differs from thermal cracking in that firing is continued until the charge is converted completely into vapors and coke. After the unit is cooled, the coke is broken up and removed by hand. Because shell-still temperatures up to 1450°F are reached in the operation, the bottom section of the still must be replaced frequently (83). These replacements and the manual handling of coke make shell-still coking a high-cost operation.

From 1913 to 1925, the Burton process, with some improvements, preponderated in the cracking field, but, out of 1200 or more that had been built, only 191 units were still in operation in 1930. This rapid obsolescence resulted from the development of furnace-type units, through which the feed was passed continuously (88). The furnace-type units were unchallenged until about 1950, when moving-bed and fluidized-bed processes were developed for some pyrolysis operations.

Furnace-type Units

Furnace-type units are used in all of the principal pyrolysis operations—from the production of ethylene to the coking of reduced crude.

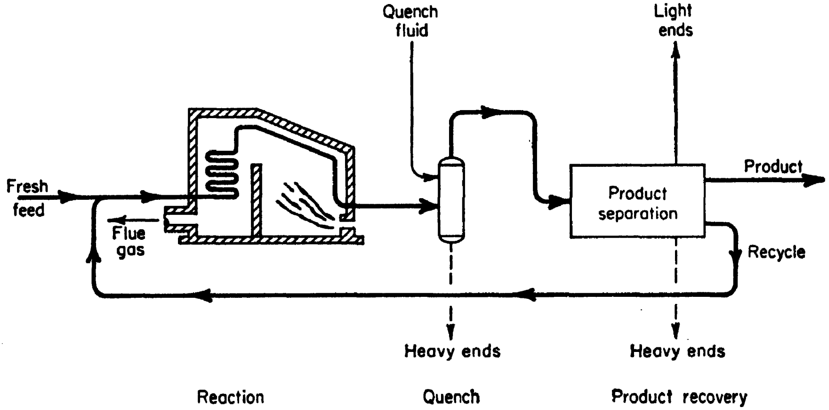

FIG. 6-7. Common features of furnace-type pyrolysis units.

Most furnace-type units are very similar, as indicated in Fig. 6-7. Fresh feed is usually combined with a recycle stream and the mixture is heated to high temperatures in the tubes of a furnace, where reaction occurs. Sometimes the furnace effluent is passed into a large "soaking drum" to increase the time for reaction. The reaction is not carried to completion. Instead, the furnace (or soaking-drum) effluent is quenched to stop the reaction at the desired point, by mixing the hot product with cold feed or a cooled recycle stream. The quenched stream is then separated (by fractionation) into light ends, product, recycle, and aromatic heavy ends, or tar. Tars are not recycled because they have great tendencies to form coke.

There are some deviations from the general pattern. Naphtha reformers are operated without recycle, and some visbreakers also. In the production of butadiene, steam was sometimes superheated in a separate furnace coil to about 1700°F and mixed with the feed; this permitted the use of lower feed temperatures, which minimized coking problems (71). However, the major deviations from the general pattern are in coking units.

Delayed-coking Units.* The furnace-type coking units are called "delayed cokers" and are so named because they heat the reduced-crude feed to coking temperatures so rapidly that little reaction occurs while the charge is in the furnace. Effluent from the furnace discharges at 900 to 975°F into a large "coke drum," where it remains until it either cracks and passes off as vapor or condenses into coke (32,47). Coke drums operate at pressures in the range of 10 to 100 psig. Because the reaction is endothermic, vapors leave the coke drum at about 800 to 850°F. When a coke drum is filled, the furnace effluent is diverted to another drum, and the coke is removed from the first one. The heaviest portion of the liquid product is of low quality as a charge to cracking; it is usually separated from the product and recycled to coking.

Decoking Equipment. Originally, coke was removed by means of cables which were arranged in helical coils in the empty drums. After a coke drum filled, its bottom head was removed, and the end of the cable was attached to a winch. Pulling the chain broke up the coke, which dropped out the bottom of the unit.

Most modern cokers employ hydraulic decoking (12), although mechanical cutters are used in some smaller units (48,83). In hydraulic decoking, high-speed water jets under high pressures bore a hole vertically through the center of the drum. Horizontal jets are then put on the revolving drilling tool, which is slowly raised through the open core to break up the coke.

Moving Beds†

Moving-bed units have been proposed for ethylene production and reduced-crude-coking operations. In both cases, the object is to avoid

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* Delayed coking was developed by the Standard Oil Co. (Indiana).

† A general discussion of moving-bed units is given in Chap. 5.

the temperature limitations of furnace-type units that result from furnace-coking problems. In coking, moving beds also permit the continuous removal of the product coke from the system.

Ethylene Production. For the production of ethylene, a "pebble heater" has been demonstrated on a pilot scale (19,35). As shown schematically in Fig. 6-8, a pebble heater is a stacked moving-bed unit, with a preheater positioned above a reactor. Pebbles—⅜-in. spheres, for example—pass down through the preheater countercurrent to hot flue gases. The preheated pebbles then pass into the reactor, where they contact hydrocarbon feed and heat it to reaction temperature. Cooled pebbles are removed from the bottom of the reactor and are carried back to the top of the preheater via a gas lift to complete the cycle. Any coke deposited on the pebbles in the reactor is burned off in the preheater. Pebble temperatures as high as 2500°F are said to be possible.

A variation of the moving-bed process has been proposed, in which only steam is superheated in the lower vessel to about 2000°F (73). The feed stream is then mixed directly with the superheated steam. Better yields are claimed as the result of better control of time and temperature. With an ethane feed, the steam required for the superheating step is about 12 lb per lb of ethylene product.

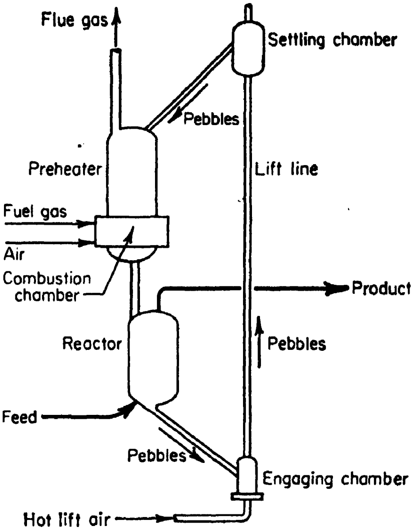

FIG. 6-8. Pebble-heater pyrolysis unit.

Coking. Two moving-bed coking processes have been developed: contact coking* in this country and the Hoechst process in Germany (36,42). In both processes the product coke particles constitute the circulating heat carrier. However, in contact coking, heat is supplied by burning part of the coke in the preheater, whereas the Hoechst process employs indirect exchange with flue gas in tubes in the preheater. Also, mass lift is used in the contact process, gas lift in the Hoechst process. Only two commercial plants employing moving beds have been reported (36,42). Difficulties were encountered in distributing the liquid feed over the moving beds of solids and in the operation of mass-lift lines, but satisfactory solutions to both problems were found (42). The basic elements of a contact coker are shown in Fig. 6-9.

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* Contact coking was developed by the Lummus Company.

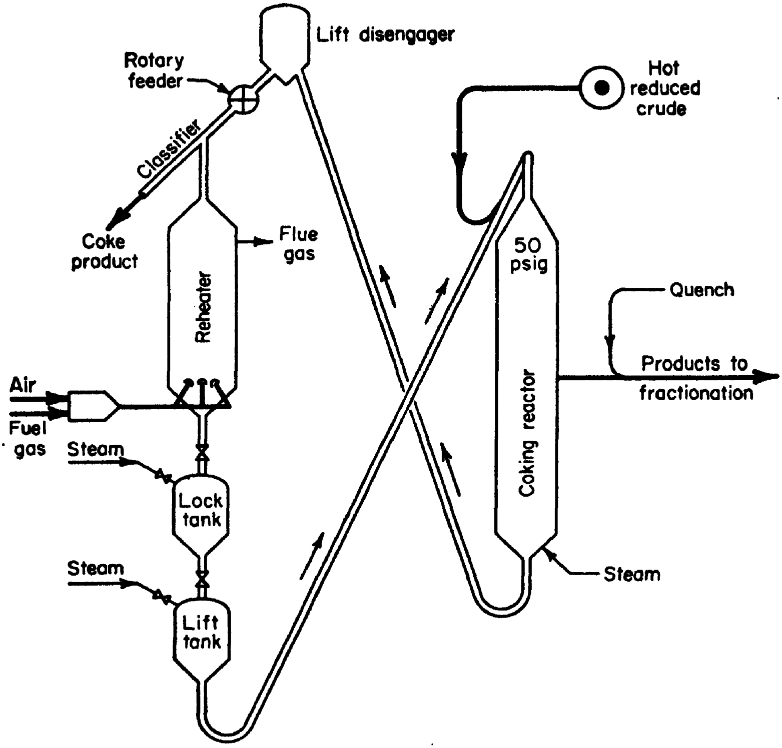

FIG. 6-9. Basic elements of a contact-coking unit.

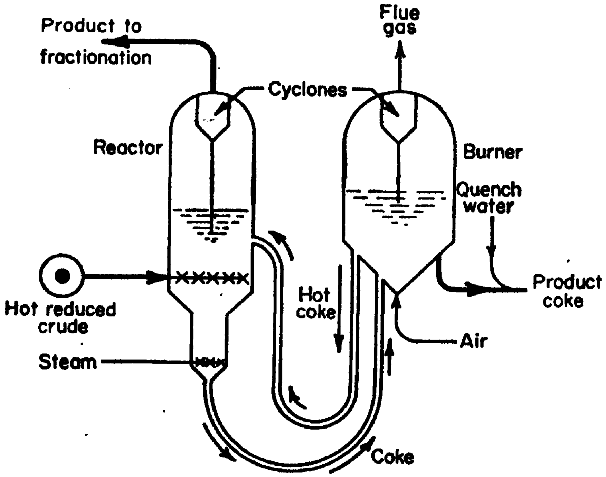

FIG. 6-10. Basic elements of a fluid coker.

Fluidized Beds*

Fluidized beds are also used in coking reduced crudes (39). As with moving beds, the product coke is circulated through a burner and a reactor, and high reaction temperatures are possible. Steam is used to fluidize the coke bed in the reactor. Typical reactor conditions are 925°F and 5 to 10 psig. Because the coke particles grow during the operation, a portion of the circulating solids may be drawn off (in addition to the net coke production), ground, and returned to the unit as "seed coke." Sufficient seed coke is recycled to hold the circulating solids in the desired size range. The size of the circulating coke may also be controlled by the use of an elutriator. The net coke production is withdrawn from the elutriator as large particles, and the finer particles are recycled to the reactor. The basic elements of a fluid coker are shown in Fig. 6-10.†

Other Pyrolysis Equipment

Other pyrolysis equipment in limited use includes regenerative refractory units for the gasification of oils‡ and for the production of carbon black; "autothermic" units for the production of ethylene, acetylene, and carbon black; electric-arc units for the production of acetylene (76); and oven units for the production of metallurgical coke. Also, molten-lead baths have been proposed for the production of ethylene (21), as has a process that mixes the feed stock intimately with hot flue gases (1).

In regenerative-refractory units, the charge is heated by passage over hot refractory materials, which were previously heated by direct exchange with flue gas. Because the refractory is cooled in the process of heating the charge, two (or more) reactors are required, with hot flue gases and charge stock alternating between them. In addition to their established uses in the gasification of oils and in the production of carbon black (23,71,79), regenerative units have been proved on a pilot scale for the production of acetylene (5,75).

In an autothermic unit, heat is supplied by burning part of the charge in air or oxygen. In this country, autothermic units have been used only for the production of acetylene and carbon black, where very high temperatures are required (5,74,75,79). In Germany, they have also had limited use in the production of ethylene (74).

Some units used in the production of metallurgical coke are bottom-fired ovens, equipped with mechanical "pushers" to discharge the coke

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* Fluidized beds are discussed in Chap. 5.

† Fluid coking was developed by the Standard Oil Co. (New Jersey).

‡ Oil is converted into gas by public utilities to supply peak-load demands and to enrich carbureted water gas.

product (13). Only heavy charge stocks—with a melting point of 200°F and a Conradson carbon of 35 per cent, for example—can be processed. Oven processes are of interest because metallurgical coke is worth considerably more than other petroleum cokes—$25 per ton versus $5 per ton in 1954. The compositions of metallurgical cokes compare with ordinary petroleum cokes as shown in Table 6-6. It is claimed that metallurgical coke can be made from high-sulfur charge stocks, but the desulfurization method is not given (13).

Table 6-6

Composition	Usual petroleum coke	Metallurgical coke
Volatile matter, wt %	8–18	4.5–8
Sulfur, wt %	0.2–4.2	0.5 or less
Ash, wt %	0.05–1.6	0.75 or less

Product Recovery

In most pyrolysis operations, the products are separated by conventional distillation; for low-pressure operations, absorption equipment is also provided to recover condensable materials from the product gases. When ethylene is the primary product, special recovery facilities are required.

The particular facilities employed for the recovery of ethylene will depend, in good measure, upon the use to which it will be put. Factors that must be considered include the removal of all sulfur compounds, the removal of acetylene, multistage compression of the product to hold temperatures below 240°F and thus avoid polymer formation, and drying of the product to avoid the formation of gas hydrates in subsequent low-temperature operations (74). Refrigerated distillation (67) is usually used to recover ethylene, but absorption and hypersorption are also employed (74).

Combination Units

Because reforming, thermal cracking, and coking (or visbreaking) operations all produce the same products, large economies were realized by combining all these operations in a single unit. As shown in Fig. 6-11, such a unit constituted almost a complete refinery in itself. Inasmuch as one larger unit is cheaper to build* and costs less to operate than two smaller units of the same capacity, large savings were realized by consolidating all the product-handling equipment. Also, large economies in heat were effected because intermediate products were not cooled and

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* Investment usually increases with the 0.6 power of capacity.

then reheated in going to and from storage. Finally, a large investment in intermediate storage was obviated. Despite all these advantages, combination units were originally considered impractical by many operators because shutting down one of the operations shuts down all the others. Operations proved the optimism of the combination-unit enthusiasts to be justified.

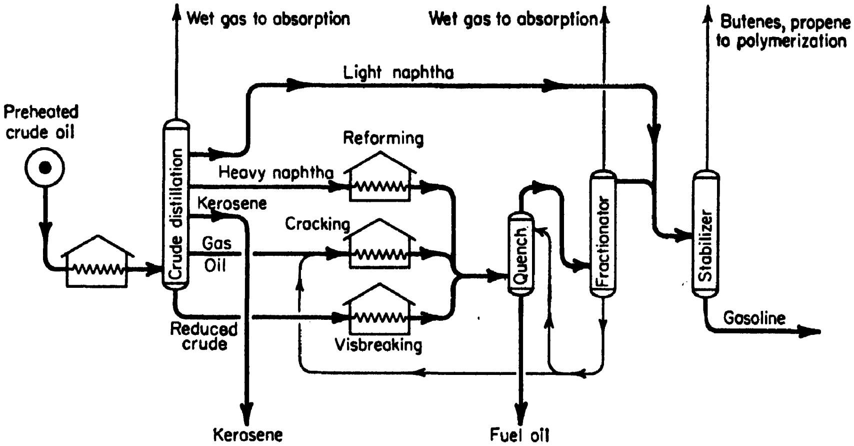

FIG. 6-11. Combination cracking unit.

PROCESS COMPARISONS

Furnace-type units continue to be the most popular type for pyrolysis, although moving-bed units are claimed to have advantages for the production of ethylene and for coking reduced crudes, and fluidized-bed units are gaining favor for coking.

Ethylene Production. For the production of ethylene, pebble heaters are "slightly more expensive" than furnace units, but they give up to 50 per cent higher yields of ethylene (35), at the expense of propene. How much the greater yield is worth will depend upon the relative values of ethylene and propene to the processor. The pebble-heater product also contains more acetylene, which may be detrimental for some uses.

Coking. A good comparison of all the coking processes is not possible from the information published in the literature. However, some generalizations can be made. Because they operate at lower pressures and higher temperatures, fluid and contact coking vaporize more of the charge and thus produce more liquid product and less coke than does delayed coking. Also, in delayed coking, lower pressures result in lower coke and gasoline yields and in higher gas-oil production. Coke yields compare as in Table 6-7.

Table 6-7

For	*Per cent of Conradson carbon in feed*
Fluid coking	110
Contact coking	110
Delayed coking (10 psig)[a]	130
Delayed coking (40 psig)	150–200

Also called Decarbonizing (Blaw-Knox Co.) (48).

The higher fluid- and contact-unit temperatures also result in gasolines of higher octane numbers (75 to 80 research octane, clear) than from delayed coking (65 research octane, clear), and in more-olefinic gases (3,42). However, gasolines produced at high temperatures are unstable and require finishing (84). Both the octane advantage and the stability disadvantage may disappear when heavy coker gasoline is charged to catalytic reforming. Some typical coking yields are given in Table 6-8

Table 6-8. Typical Coking Yields

	Type of coking				
	Delayed (31)	Contact (42)	Fluid (31)		
Charge stock:					
Gravity, °API	15	18.9	15	15.2	4.2
Conradson carbon, wt %	9	11.7	9	14	24
Sulfur, wt %	1.2	0.6	1.2	0.9	4.3
Yields:					
Dry gas, wt %	6	14.5	5.5	8	9.5
Butanes, butenes, vol %	2.5	22.0	1.5	2.5	3.5
Gasoline, vol %	22.5		13	21.5	19.5
Gas oil, vol %	57	51.0	75	61	52
Coke, wt %	22	12.5	11	16	27.5
Gasoline:					
Research octane, clear	69.9	76.5	76.3	73	77
Sulfur, wt %	.....	0.1	0.3	0.2	0.9
Gas oil:					
Characterization factor	.....	11.85	11.59	11.55	11.17
Sulfur, wt %	0.93	.....	1.4	0.5	3.7
Conradson carbon, wt %	0.0	.....	1.1	2.1	2.8

INVESTMENT AND OPERATING COSTS

Costs for pyrolysis units have been published for units producing ethylene (or ethylene and propene), for units producing acetylene, and for coking units.

Ethylene Production. Investment and operating costs were published in 1956 for the production of ethylene from crude oil and from refinery gas. A plant to produce 80,000,000 lb per year of ethylene from crude oil was quoted at $10,000,000, and the direct operating costs were estimated at 2.4 cents per lb of ethylene (55). For a plant charging a typical refinery gas and producing 200,000,000 lb per year of ethylene and 95,000,000 lb per year of propene, the investment was quoted at $9,900,000, and direct operating costs were estimated at 2.4 cents per lb of ethylene and propene combined (54). The major part of both these costs is for product-recovery equipment.

Acetylene Production. Various estimates for the production of acetylene have been published (5,30,76). For a regenerative-refractory (Wulff) process, an investment cost of 6 to 7 million dollars was indicated for a 50 million-lb-per-year plant in 1954, with a manufacturing cost of about 5 cents per lb (5).

Coking. Among coking units, the fluid type appears to have a decided investment advantage. In 1954, a 2,500-bbl-per-day delayed coker was quoted at $2,100,000, a contact coker for the same operation at $1,600,000 (42). In 1956, a 10,000-bbl-per-day fluid coker was quoted at $2,300,000 (62). Presumably, for units of equal size, operating costs for all processes would be in the same range. The coke from a fluid unit is hard to pulverize for use as a power-plant fuel, but test data (11) indicate that the penalty for this disability should be small.

DESIGN OF PYROLYSIS EQUIPMENT

The design of pyrolysis equipment is a difficult procedure, especially for furnace-type units.* Fortunately, a precise design is needed only for ethylene- and acetylene-producing units, for which very high temperatures are required because of equilibrium considerations. Because reactions proceed rapidly at the required temperatures, precise control of the time-temperature relationship is necessary to avoid overtreating, with a consequent loss of product via side reactions. With the exception of carbon-black production, other pyrolysis operations operate at lower temperatures, where reaction rates are lower and control of time-temperature relationships is less critical. In the production of carbon black, side reactions are no problem because the feed is converted to the ultimate product. All furnace units must be designed, of course, to avoid excessive coke formation in the tubes. Provisions must also be made for removing the coke that does form.

Ethylene Production. The design of furnace units for ethylene production is a trial-and-error procedure, primarily because of pressure-drop considerations, which affect, and are affected by, the temperature-con-

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* However, the situation is much improved from the time of the first designs of pyrolysis equipment, when "design" capacities were set *after* units were operated.

version relationships. Systematic procedures have been developed (22,50,72,77), which simplify the design of pyrolysis furnaces. Recommended design factors (10,70,72,77) include mass velocities of 20 to 35 psf per sec, a continuously rising temperature gradient graduated to give only a slight rate of increase near the outlet of the coil, a coil-outlet pressure of 5 to 15 psig, tube diameters of 4.5 in. or less, the use of high alloys (Inconel, Incoloy, and 25-20 stainless steel) for the higher-temperature furnace tubes, and the use of parallel furnaces to permit decoking of furnace tubes without going off stream.

The design of a pebble-heater unit should be relatively straightforward, inasmuch as pressure drop through the reactor should be low.

Reforming, Cracking, and Visbreaking. The designing of pyrolysis coils for reforming, cracking, and visbreaking follow the same lines. The designer first selects the severity of treatment desired, then determines the "soaking factor" required, and finally sets the furnace conditions. Soaking factor* is a function of temperature and reaction time, which correlates the extent of reaction. Inasmuch as the soaking factor doubles for each temperature increase of 25 to 30°F, it is not necessary to specify operating temperatures precisely. Rather, the optimum temperature is determined in the actual operations of each commercial unit.

In gas-oil cracking, conversions per pass range from 15 to 23 per cent (27), and the unconverted gas oil is often "recycled to extinction," except for the heaviest material, which is rejected as "tar." Tar is excluded from the recycled material because it promotes the formation of coke.

The design of vapor-phase cracking units has been discussed by Schutt (69); a more general discussion of pyrolysis designs is given by Nelson (45).

Coking. In coking, a large share of the cost of furnace units is associated with the coke drums. They are usually designed for a 48-hr cycle—24 hr for coking and 24 for decoking—although the decoking operation can be carried out in a shorter time (57,83). Throughout the coking operation, the preheated feed is usually charged to the bottom of the drum, although top entry may be used (83). As a consequence, a

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* Soaking factor is

$$F = \frac{C}{V}\int_0^1 \frac{P_T}{750} \times \frac{K_T}{K_{800}} \times dZ$$

where C = coil volume above 800°F
F = daily throughput in barrels
P_T = pressure at temperature T
K_T, K_{800} = reaction-velocity constants based on an activation energy of 53,400 cal per g mole
Z = fractional coil volume above 800°F

layer of froth forms above the coke (57,87). To avoid carry-over of foam with the overhead vapors, coke drums are designed with "outages" above the design coke level of at least 10 ft. Gamma rays are sometimes used to detect coke levels (58,87). Coke densities vary during the operation, and final coke densities for bottom-entry operations are about 55 lb per cu ft (87).

The vapor rates from a delayed coker fluctuate somewhat through a coking cycle, and the product-recovery equipment must be designed for the maximum rates.

Little information has been published on the design factors for moving-bed coking units except that reactor outlet temperatures are 900 to 1000°F, maximum coke temperatures are about 100° higher, 150-lb steam is specified for the mass-lift system, and 14 lb of coke are circulated per pound of oil charged (42).

Fluid cokers are designed for reaction temperatures of about 950°F and reheater temperatures of about 1125°F (39). Vessel-top pressures are about 5 to 10 psig. Feed is injected into the reactor at 500 to 700°F through multiple steam-atomizing nozzles. To ensure fluidization of the bed, steam is injected below the grid, and steam constitutes about 65 to 70 per cent of the effluent vapors (53). A single stage of cyclones is used in the reactor, two stages in the regenerator (39). To minimize coke formation in the overhead equipment, the quench fractionator may be located directly above the coking unit. An 8-in. refractory lining is used in the reaction vessel (double the usual lining) to compensate for coke deposition within the lining, which reduces its insulating value. The circulating coke is predominantly 150 to 400-μ material (*7a*), and superficial gas velocities are in the range of 2 to 5 fps (53).

Coking and Decoking of Furnace Tubes. Coking in furnace tubes is a function of the charge and the furnace conditions. Inasmuch as coking of tubes is a surface phenomenon, it depends upon the characteristics of the surface film. Because low velocities are conducive to coking, steam is often injected to increase them (57,64). Coking difficulties are most likely at the point where heavy stocks are completely vaporized in a furnace, presumably because liquid hydrocarbons carry coke (or incipient coke) along with them.

Coke is removed from furnace tubes by drilling it out or by controlled combustion in a steam-air mixture. There are advantages for both methods, but the steam-air technique is usually preferred, at least where substantially all of the deposits are combustible. Steam-air decoking is usually both quicker and cheaper (59,84). Frequently, furnace tubes can be installed with welded return bends when steam-air decoking is to be used, and this feature saves investment in comparison with the usual header designs.

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CHAPTER 7

CATALYTIC CRACKING

Catalytic cracking has written one of the most remarkable chapters in the history of petroleum refining. Within a few years of its first successful application in 1936, it became the largest of all catalytic operations—a position it has since retained. Further, it has fostered the development of new engineering techniques, the use of which has spread to many other processes, both within and outside the petroleum industry.

Background

Until the Burton process was proved commercially, many technologists thought that thermal-cracking conditions were too severe for the riveted-and-caulked vessels then in use. Catalysts were sought, therefore, to promote the reaction, and, thus, to permit the use of lower temperatures and pressures.

McAfee Process. The quest for cracking catalysts bore early fruit, and the first catalytic-cracking unit went on stream in 1915—just two years after the first thermal unit was completed. Developed by A. M. McAfee (36) and commercialized by the Gulf Refining Company, the process employed aluminum chloride as the catalyst. In the presence of aluminum chloride, gas oils crack at 500 to 550°F, and atmospheric pressure may be used. In contrast, early thermal-cracking units required at least 750°F and about 85 psi. The commercial McAfee unit performed as expected, except that difficulties were experienced in recovering the expensive catalyst from the tarry residue of the process. On the other hand, new welding techniques were developed rapidly for constructing equipment to withstand high temperatures and pressures, and their development eliminated the major incentive behind the McAfee process. Consequently, the McAfee process never became important.

Houdry Process.* The first successful catalytic cracking process was commercialized about twenty years later. Developed by Eugene Houdry

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* The Houdry process was developed by the Houdry Process Corp., Socony-Vacuum Oil Co., and Sun Oil Co.

and coworkers (3), the process employed activated clays as catalysts. It had been recognized earlier that such materials would catalyze the cracking of heavy oils to yield more and better gasoline; however, the catalyst deactivates rapidly because of the deposition of tarry materials ("coke") on the catalyst. Houdry found that the activity could be restored by burning the coke off at controlled temperatures. Although this discovery paved the way for the development of catalytic cracking, major obstacles had to be overcome before the process could be commercialized.

Under cracking conditions, clay catalysts are deactivated in minutes. If the catalyst is employed in fixed beds, short reaction periods must be used, after which the catalyst must be regenerated; a 10-min reaction period is typical. In commercial units, several reactors must be provided so that the feed may be switched cyclically from a deactivated reactor to an active one. Moreover, the cracking reaction is endothermic, while the regeneration of the catalyst is very exothermic. Means must be supplied, therefore, to heat the catalyst during reaction and to cool it during regeneration. During regeneration, the reactor surfaces are exposed to severe oxidation conditions, during reaction, to reducing conditions. The alternation of atmospheres necessitates special materials of construction, especially if the feed is high in sulfur, some of which is deposited with the coke and oxidized to corrosive SO_2 and SO_3 during regeneration. These were all serious problems, and their solution was a major achievement.

The first commercial Houdry unit went on stream in 1936, and the process was an immediate success. By 1941, 16 units were on stream or under construction. Before the process was rendered obsolete by the development of fluid and moving-bed processes, 29 Houdry units were built, with a combined capacity of 375,000 bbl of charge stock per day (3).

Circulating-catalyst Processes. The first fluid-cracking units went on stream in 1942; the first moving-bed unit one year later. In both types of units, solid catalysts are circulated continuously through a reactor and a regenerator. The substitution of circulating catalyst for fixed beds avoided many problems inherent in the Houdry process. These included:

1. A complicated and expensive system of automatic valves for control of the cyclical operations
2. Complicated temperature-control devices, which consisted of closely spaced tubes in the reactors, through which molten salt was circulated to heat the catalyst during reaction and to cool it during regeneration
3. Catalyst charging and discharging problems that resulted from the closely spaced tubes

4. Use of expensive alloys that were needed because of alternating oxidizing and reducing atmospheres
5. Variations in the composition of the product through the cycle, which increased the cost of recovery equipment

Circumvention of these problems accelerated the growth of catalytic cracking. By 1957, the installed capacity in the United States was about 4 million bbl of charge stock per day.

Other Processes. Two other catalytic cracking processes are worthy of mention—Cycloversion (72) and Suspensoid cracking (78). Cycloversion is a fixed-bed process employing a rugged bauxite catalyst under such conditions that process cycles of 6 hr, or longer, may be used. Regeneration temperatures as high as 1400°F are permissible. A 10,000-bbl-per-day unit was placed on stream in 1944. Although it was considerably simpler than the earlier Houdry process, Cycloversion did not catch on, probably because of the concurrent development of the fluid-bed and moving-bed processes.*

The Suspensoid process (22) employs the original idea for cracking with powdered catalyst. A small amount of catalyst (2 to 3 lb per bbl) is charged with the feed to a furnace similar to the furnaces in thermal-cracking units, and the spent catalyst is filtered from the products and discarded. Because only a small amount of catalyst is used, its catalytic effects are small. However, the catalyst permits the use of higher temperatures than would otherwise be tolerable, because it adsorbs some of the coke, and it scours much of the rest out of the furnace tubes (68). Higher octanes result from the use of higher temperatures. Typical reaction conditions are 1050°F and 500 psig. Imperial Oil, Ltd., converted some thermal-cracking units to Suspensoid cracking about 1940.

Development of Fluid Cracking Units†

Despite the large-scale use of the fluidized-solids technique in catalytic cracking, the phenomenon is not fully understood. Fundamental research is only now being done to elucidate it. Even so, much less was known about fluidized solids at the time that the first units were built.‡ Advances have been made since then that simplified the design and reduced investment and operating costs. In 1955, investment costs were estimated to be one-third of the cost to duplicate the original units (*22a*).

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* Cycloversion was developed by the Phillips Petroleum Co.

† The fluid cracking process was developed by the Standard Oil Co. (New Jersey) in collaboration with Standard Oil Co. (Indiana), the M. W. Kellogg Company, and a number of others.

‡ The principles of fluidized beds are discussed in Chap. 5.

Original Design. The original design is shown in Fig. 7-1. Gas oil, preheated in a furnace, was charged to the reactor inlet line, where it picked up regenerated catalyst from a regenerated-catalyst standpipe and carried it into the reactor. Catalyst carried overhead by the effluent vapors was separated by means of cyclones. It then flowed by gravity into an aerated hopper and through aerated standpipes to the spent-catalyst transfer line. There it was picked up by air and carried into the regenerator, where coke was burned off. Catalyst carried out with the flue gas was separated by means of cyclones, and returned to the reactor inlet line through a second aerated hopper and standpipe. To remove heat from the regenerator, part of the catalyst withdrawn from the regenerator hopper was circulated through a tubular cooler and back to the regenerator. Flow of catalyst through the unit was controlled by means of slide valves in the standpipes.

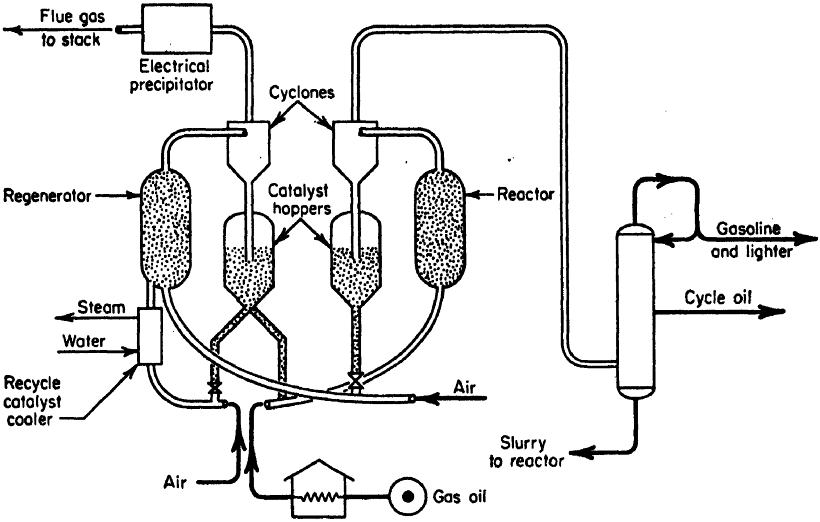

FIG. 7-1. Original fluidized-bed design.

From the regenerator cyclones, flue gas passed through an electrical precipitator to recover catalyst fines, which were returned to the regenerator. Reaction products passed into a distillation column, in the bottom section of which they were quenched to about 600°F to condense the heaviest hydrocarbons. Quenching was accomplished by circulating heavy condensate through a cooler and then back through the bottom section of the column, and the circulating condensate scrubbed catalyst fines out of the upflowing reaction products. The catalyst slurry so produced either was returned directly to the reactor or was sent to a settler to concentrate the catalyst, the concentrated bottoms being returned to the reactor. (Settling minimizes the return of high-coke-forming heavy ends (41,59).) In the upper part of the column, the scrubbed reactor effluent was separated into gas, unstabilized gasoline, and light and heavy cycle oils.

Limitations of Original Design. In the first fluid units, circulation of catalyst was limited by the fact that all the circulating catalyst had to pass through two sets of cyclones. By limiting the catalyst circulation, this restriction limited the amount of heat that the catalyst could transfer from the regenerator to the reactor. Consequently, much of the heat of combustion was removed from the regenerator by circulating catalyst through the recycle-catalyst cooler, and much of the heat required in the reactor was supplied by preheating the feed. Thus, early units operated under the anomalous situation of preheating the feed, cooling the regenerated catalyst, and then mixing the two streams before charging them to the reactor.

To ensure against reversals of flow during an upset, the slide valves of early units were designed for large pressure drops; tall standpipes were required and an expensive structure was needed to support the vessels at the high levels required.

Process Improvements. The first major advance was made when it was found that a fluidized catalyst could be held in a vessel as a dense phase that resembles a liquid and that catalyst could be withdrawn from the dense phase through a standpipe. This discovery removed the restriction on catalyst-circulation rates, and catalyst could be circulated fast enough to transfer all the recoverable regeneration heat to the reactor. Although regeneration requirements increase somewhat as the rate of catalyst circulation is increased (43), transferring the heat of combustion to the feed simplifies the design by eliminating the need for catalyst coolers and feed preheaters.

With the loads on the cyclones reduced, they could be placed inside the reactor and regenerator; this move simplified piping and solved mechanical problems inherent in the original design. Subsequently, operating experience proved that electrical precipitators were not essential, and they were omitted from many of the later units. More recently, U-bends have replaced standpipes in some units, and higher velocities have been used in the catalyst vessels; also stacked vessel arrangements have been employed (58). In 1956, a two-stage unit was announced; such a unit is more costly to build, but is claimed to give superior yields (25).

Development of Moving-bed Processes*

The possibilities of moving-bed operations were recognized early, and a pilot unit was built in Llandarcy, Wales, in 1939. However, the

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* The principles of moving beds are discussed in Chap. 5.

Anglo-Iranian Company (now British Petroleum), which built the plant, abandoned the development at the outbreak of World War II. Meantime, the Houdry Corporation, in collaboration with the Sun Oil Co. and Socony-Vacuum Oil Co., had also been working on a moving-bed process. As a result of their work, the first successful moving-bed unit went on stream in 1943.

Original Design. The first process employed a Thermofor kiln* for regeneration; consequently, it was called the Thermofor catalytic cracking, or TCC, process (48). In the regeneration kiln, coke was burned off the downflowing catalyst in seven to ten stages. Between stages, the catalyst was cooled by passage over cooling coils. Countercurrent flow of vapors and catalyst was used in the first units, and bucket elevators were employed to convey catalyst to the tops of the reactor and regenerator. From a mechanical standpoint, the design of elevators to handle large loads of catalyst at temperatures as high as 1000°F was a difficult problem, as was the lubrication of them. Graphite was used as a lubricant.

Limitations of Original Design. Although the original TCC process was a major improvement over the Houdry process, it had two limitations: it could handle only vaporized feeds, and, because of the high cost of the elevators, catalyst circulation was limited; therefore, only a fraction of the heat of combustion could be transferred to the reactor with the regenerated catalyst.

Process Improvements. The feed-stock limitation was removed when a method was developed for distributing liquid and mixed liquid-vapor streams uniformly over the moving catalyst, and concurrent flow of reactants was substituted for countercurrent (52). In addition to extending the utility of the process, this change permitted elimination of the tar separator, in which the feed to earlier units was flashed to ensure that no liquid reached the catalyst.

The catalyst-circulation limitation was relaxed when a pneumatic, or gas-lift, system was developed to replace elevators for the circulation of catalyst (52). At the higher circulation rates permissible with a gas-lift system, much of the heat of combustion can be transferred from the regenerator kiln to the reactor. This change simplified the design by reducing both the cooling load in the regenerator and the feed preheating and vaporizing load. In gas-lift units, the regenerator kilns are built with only one to three stages, as compared with seven to ten stages previously provided in TCC units.

Present Designs. Two types of gas-lift units have been developed: the Houdriflow (52) and the Airlift TCC (58). The principal features

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* The Thermofor kiln had been developed previously by the Socony-Vacuum Oil Co. for the regeneration of clays used in treating lubricating oils.

of these units, which are very similar, are illustrated in Fig. 7-2. The reactor is located above the kiln. (Reactor and kiln may be separate vessels, as shown, or they may be combined into a single structure.) Catalyst flows by gravity from a "disengaging hopper" to the reactor through a seal leg. The hopper operates at atmospheric pressure, the reactor at 5 to 10 psig, and the differential between them is maintained by a current of steam flowing upward through the seal leg, countercurrent to the flow of catalyst. An excess of steam is used, and some passes down with the catalyst and prevents hydrocarbons from passing up and escaping through the catalyst hopper. Catalyst entering the reactor is contacted with the hydrocarbon feed, which is distributed over the catalyst through an atomizing spray nozzle. Products are taken off near the bottom of the reactor. Below the product draw-off, the down-flowing catalyst is stripped by an upflowing current of steam to remove hydrocarbons; stripping steam passes out of the reactor with the products. Additional steam passes down with the catalyst through a seal leg to the kiln, which operates only slightly above atmospheric pressure. The pressure differential between the reactor and regenerator is maintained by the steam flowing through the intermediate seal leg. In the regenerator, coke is burned in one or more burning stages. If more than one stage is used, the catalyst is cooled between stages by passage over cooling coils. In Houdriflow units, flow of regeneration air is countercurrent to the flow of catalyst, and each burning zone has its own air supply and flue-gas outlet. In Airlift units, two burning zones are used, with countercurrent flow of air in the upper zone and concurrent flow in the lower zone; cooling coils are provided between the stages. In Houdriflow units, a mixture of flue gas and steam is used to lift the catalyst, 100 psi steam being used to compress flue gas to 5 to 6 psig in an educator-type thermocompressor. In Airlift units, the lifting medium is air at 2 psig.

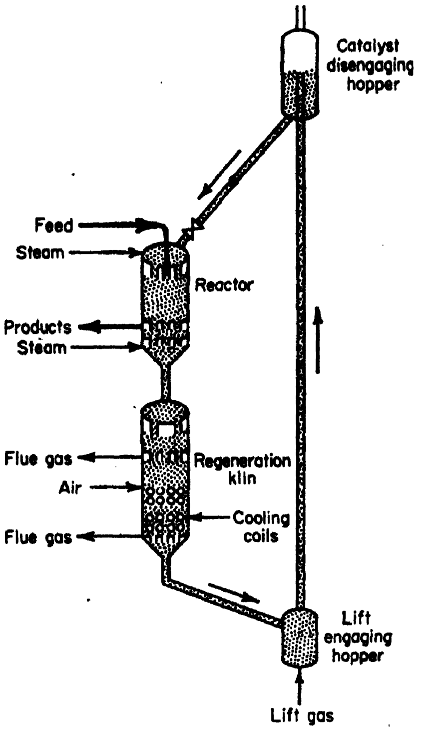


Fig. 7-2. Schematic diagram of a gas-lift moving-bed catalytic-cracking unit.

In order to prevent the buildup of catalyst fines in moving-bed units, a slip stream of the circulating catalyst is passed through elutriation equipment from which material finer than 14 mesh is discarded (48). Catalyst losses may be in the range of 0.03 to 0.05 per cent of the circulation rate, or about 0.3 to 0.7 lb per bbl (4).

Reaction Patterns

In catalytic cracking, there are two basic reaction patterns. One applies to paraffins, olefins, and naphthenes; the other to aromatics. Hydrogen-transfer reactions are also important. The over-all reaction is endothermic to the extent of 90 to 200 Btu per lb of cracked products (48).

Cracking of Paraffins, Olefins, and Naphthenes (23). How paraffins, olefins, and naphthenes crack over the usual catalysts is illustrated in Fig. 7-3, which shows the products from cracking cetane, cetene, and amyldecalins. Three points stand out. Most striking is the preponderance of 3-carbon and 4-carbon products, which, together, range from 0.9 to 2.2 moles per mole of feed cracked. Next is the small amount of methane and ethane produced. Finally, there are no products higher boiling than the feeds, except, of course, for the coke deposited on the catalyst. In all three points, catalytic cracking differs from thermal cracking.

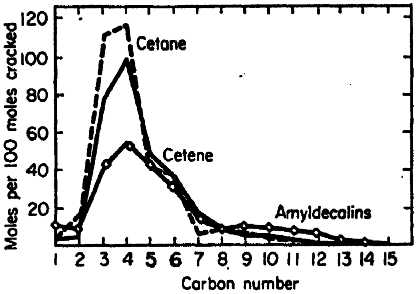
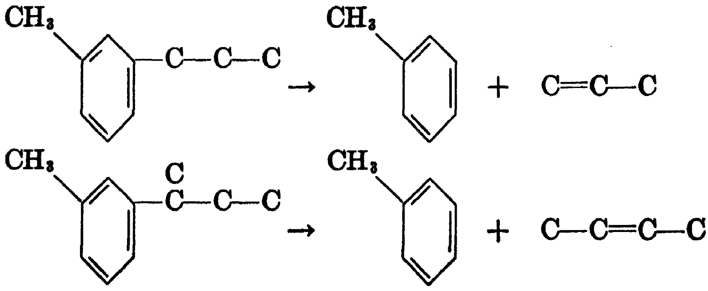


FIG. 7-3. Products from cracking of nonaromatic hydrocarbons (23).

Cracking of Aromatics (23). Aromatic rings are stable under the conditions of catalytic cracking, just as they are under thermal-cracking conditions. However, long alkyl chains are reactive. The predominant primary reaction of alkyl chains is scission from the aromatic ring, to yield olefins. For example,



Little benzene is formed, inasmuch as the methyl group is tightly held. The ease of cracking of alkyl aromatics increases with the length of the side chain, at least up to a length of four carbon atoms.

Hydrogen-transfer Reactions and Coking. Paraffinic products from catalytic cracking are considerably more branched than would be expected from equilibrium considerations. By way of example, butanes and pentanes contain only 10 to 20 per cent of the normal isomers. One explanation may be found in hydrogen-transfer reactions between naphthenes and tertiary olefins (9):

$$\begin{tikzcd}
n\text{-olefin} + \text{decalin} \arrow[r] \arrow[d, shift right] & n\text{-paraffin} + \text{tetralin} \arrow[d, shift right] \\
i\text{-olefin} + \text{decalin} \arrow[r] \arrow[u, shift right] & i\text{-paraffin} + \text{tetralin} \arrow[u, shift right]
\end{tikzcd}$$

Because the reactions of olefin isomerization and of hydrogen transfer between *i*-olefins and decalin are much faster than the other reactions, *i*-paraffins are produced much faster than *n*-paraffins.

Coking tendencies of feed components increase in the order: paraffins, naphthenes, and aromatics, and the coking tendencies of aromatics increase with the number of condensed rings (82). Coking of naphthenes is associated with hydrogen-transfer reactions (9).

Reaction Mechanism (23)

In contrast to thermal cracking, which occurs by virtue of chain reactions of neutral free radicals, the intermediate reaction products in catalytic cracking are positively charged fragments called "carbonium ions." (A carbonium ion differs from a free radical in that it contains one less electron.) Carbonium ions are participants in the catalytic cracking of all classes of hydrocarbons, although they are not believed to participate in hydrogen-transfer reactions (9).

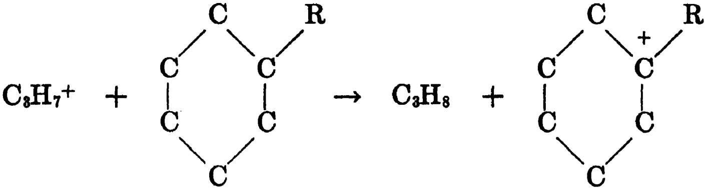
Formation of Carbonium Ions. A carbonium ion results from the addition of a proton to an olefin, and it is this reaction that initiates the chain reactions in catalytic cracking. A typical reaction is

$$CH_3{-}CH{=}CH_2 + H^+ \rightarrow CH_3{-}C^+H{-}CH_3$$

When the feed stock contains no olefins, some must be produced by thermal cracking before catalytic cracking can begin. As a consequence, feeds that contain olefins crack more readily than feeds that do not include them.

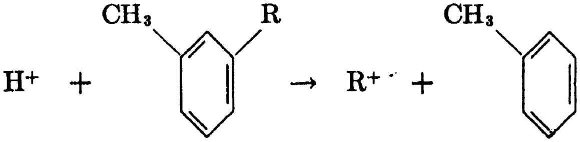
Once formed, carbonium ions can exchange hydride ions with paraffins or naphthenes:

$$C_3H_7^+ + CH_3{-}CH_2{-}(CH_2)_n{-}CH_3 \rightarrow C_3H_8 + CH_3{-}C^+H{-}(CH_2)_n{-}CH_3$$



By this exchange reaction, paraffins and naphthenes are made reactive.

Aromatics are unique in their catalytic reactions. A typical reaction is believed to go as follows:



According to this scheme, no aromatic carbonium ion is formed. Rather, one positively charged group is expelled from the aromatic nucleus as another one enters. The ease of expelling an alkyl ion increases in the order methyl, ethyl, isopropyl, and tertiarybutyl.

Reactions of Carbonium Ions (23). Thermodynamically, secondary and tertiary carbonium ions are more stable than primary ones.* Thus, carbonium ions are formed as either secondary or tertiary ions, or they isomerize immediately to those isomers.

A carbonium ion reacts to form an olefin by loss of a proton or a smaller carbonium ion:

$$CH_3{-}C^+H{-}CH_2{-}R \rightarrow CH_3{-}CH{=}CH{-}R + H^+$$
$$CH_3{-}C^+H{-}CH_2{-}R \rightarrow CH_3{-}CH{=}CH_2 + R^+$$

In both reactions, a charged particle is produced to continue the chain reaction.

When a large carbonium ion breaks down to form an olefin and a smaller ion, the charged carbon of the original ion becomes part of the olefinic linkage, and an adjacent secondary carbon becomes the other

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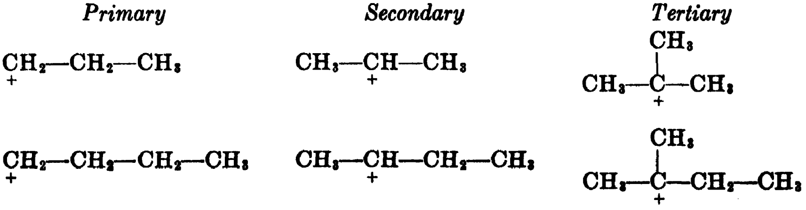
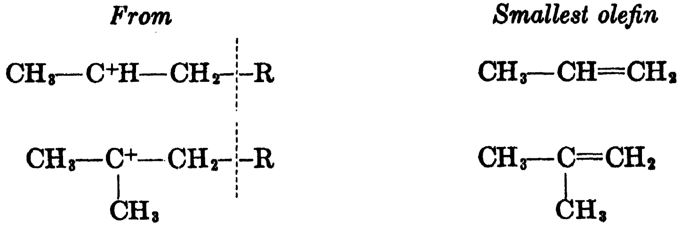
* Examples of carbonium ions are as follows:



Primary	*Secondary*	*Tertiary*
$\underset{+}{C}H_2{-}CH_2{-}CH_3$	$CH_3{-}\underset{+}{C}H{-}CH_3$	$CH_3{-}\underset{+}{\overset{CH_3}{C}}{-}CH_3$
$\underset{+}{C}H_2{-}CH_2{-}CH_2{-}CH_3$	$CH_3{-}\underset{+}{C}H{-}CH_2{-}CH_3$	$CH_3{-}\underset{+}{\overset{CH_3}{C}}{-}CH_2{-}CH_3$

olefinic carbon atom. Propene and *i*-butene are the smallest olefins that can result.



From *Smallest olefin*

$$CH_3—C^+H—CH_2—\vdots—R \qquad CH_3—CH{=}CH_2$$

$$\underset{\displaystyle CH_3}{\underset{|}{CH_3—C^+}}—CH_2—\vdots—R \qquad \underset{\displaystyle CH_3}{\underset{|}{CH_3—C}}{=}CH_2$$

This mechanism explains the low yields of methane and ethane in catalytic cracking. As shown in Fig. 7-4, yields calculated on the basis of this mechanism check closely with the experimental yields in the cracking of cetane.

In the cracking of larger carbonium ions to form smaller ions and olefins, the smaller ions tend to isomerize to secondary or tertiary structures. Thus, branched chains predominate in cracked products, even when the feed is made up of straight-chain hydrocarbons.

Catalysts

Cracking catalysts are solid materials with acidic properties. Because reactions take place only on their surfaces, high porosity is necessary;* typically, a catalyst may contain 50 to 55 per cent voids in the form of micropores. Because catalysts cycle rapidly between reaction zones and burning zones, they must also be resistant both to abrasion and to temperature changes. The first catalysts were acid-treated clays; these "natural" catalysts are still used in substantial quantities, although "synthetic" catalysts are now more popular.

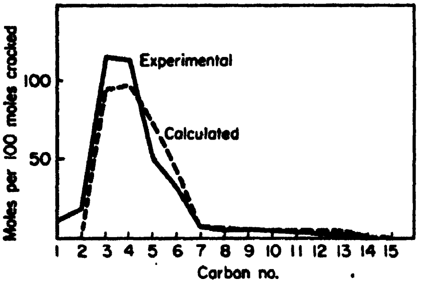


FIG. 7-4. Predicted and experimental yields from cracking cetane (23).

Catalyst Compositions. Natural catalysts are composed principally of silica and alumina, but they contain significant quantities of other materials, some of which may be deleterious in certain circumstances. Synthetic catalysts, on the other hand, are made from high-purity chemicals, and their compositions are controlled rigidly. All present synthetic catalysts are silica-alumina, but a silica-magnesia version has been produced. Typical compositions are given in Table 7-1.

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* Fresh synthetic-alumina catalyst has a surface area of about 500 sq meters per gram or about 56 acres per lb (73).

Table 7-1. Typical Compositions of Cracking Catalysts

	Natural catalysts			Synthetic catalysts		
	Bentonite	"SR"	Kaolin	Low-alumina	High-alumina	SiMg
Ignited basis, %:						
Al_2O_3	18	40	45	13	25	
SiO_2	74	60	53	87	75	
MgO	5	....	...	....	....	30
CaO	3	....	...	0.01	0.01	
Fe_2O_3	2	0.2	0.3	0.05	0.05	
Na_2O, K_2O	0.3	0.04	...	0.02	0.02	
Dry (220°F) basis, %:						
Ignition loss at 1600°F	9	....	2.0			
SO_4	4	2	0.1	0.4	0.4	

The high-alumina catalysts, which were developed about 1955, are said to be more stable both mechanically and catalytically than the low-alumina type (34,51,73), and they may also be somewhat more selective for the production of gasoline (67).

Catalyst Forms. For use in moving-bed units, catalysts were first made in the form of pellets, usually 4 mm in each dimension (3). Natural catalysts are still supplied in that form, but the synthetic varieties are produced as beads, about 3 mm in diameter, which have superior mechanical properties (58,65). For use in fluidized-bed units, both the natural and synthetic catalyst were originally supplied as ground powders. However, most of the synthetic production is now in the form of microspheres. Like their counterparts for moving-bed operations, microspheres have superior mechanical properties, and they are also said to be less erosive (6). Several grades of fluid catalysts are produced. Fine grades are used in units equipped with electrostatic precipitators; most other units employ coarser catalysts (73). Typical size distributions are given in Table 7-2.

Table 7-2

	Per cent by weight	
	Fine grade	Coarse grade
0–20 μ	14	2
20–40 μ	28	10
40–80 μ	44	60
80+ μ	14	28
Retained on 100-mesh sieve	1	2

Relative Performances. Different yields are obtained from the different cracking catalysts as indicated in Table 7-3 for 50 per cent conversion of a gas oil at 900°F in a fluidized-bed operation (15). Silica-magnesia gives the highest gasoline yields, silica-alumina gives the highest octane product, and bentonite clays are intermediate in both respects. Silica-magnesia also gives higher yields of gas oil in the boiling range of distillate fuels.

Table 7-3

	Silica-alumina	Bentonite clay	Silica-magnesia
10 lb RVP gasoline, vol %	43.0	46.5	49.0
Coke, wt %	4.2	4.4	4.1
Gasoline octane (3 cc TEL)			
Research	95.8	94.7	92.8
Motor	82.8	83.5	82.9

A catalyst produced from kaolin clay was introduced in 1957 (7). It is said to be generally similar in performance to synthetic silica-alumina catalysts. Advantages claimed over synthetic catalysts are a somewhat higher gasoline yield, greater stability, and lower cost.

Regeneration Properties. With regard to regeneration of catalysts, two properties are important—the rate of burning and the CO_2/CO ratio in the flue gas.

Rates of burning have been satisfactory with all commercial catalysts except silica-magnesia. On aging in a commercial unit, the rate of burning with silica-magnesia declined steadily, and eventually limited the coke-burning capacity of the unit (15).

The CO_2/CO ratios in the flue gases are important for two reasons. First, higher ratios reduce the amount of coke that can be burned in a given volume of air, and most units are limited by regeneration-air capacity. On the other hand, high CO concentrations tend to promote "afterburning" of the CO above the catalyst, which can result in destructively high temperatures. The usual CO_2/CO ratios are as follows:

Catalyst	*CO_2/CO ratio*
Silica-alumina	1.0–1.2
Silica-magnesia	1.6–2.0
Bentonite clay	1.7–2.2

In fluidized-bed units, lower CO_2/CO ratios are usually preferred. For moving-bed units, on the other hand, a small amount of chromium is sometimes added to promote complete burning to CO_2, and thus to obviate the possibility of afterburning (79).

In fluid units, maximum regeneration temperatures are about 1100°F (61), although temperatures as high as 1150°F are used. In moving-bed units, maximum temperatures are 1150 to 1400°F (6*a*,58,65).

Poisoning of Catalysts. All cracking catalysts are poisoned by metals. Various nitrogen compounds are temporary poisons, and some sulfur compounds are poisons in some circumstances.

Any metals contained in feed stocks to catalytic cracking tend to be picked up by the catalyst. Metals of the reducible-oxide group are most troublesome, especially iron, nickel, vanadium, and copper (17,29, 40,75); such metals lower gasoline yields and increase the production of coke. Salts such as sodium chloride deactivate the catalyst, but do not necessarily change its selectivity. When a metals-free feed is cracked over a contaminated catalyst, its performance improves, presumably because the contaminants deactivate more rapidly than does the basic catalyst. The following limits have been suggested for feeds to fluid units (21): iron, 1 ppm; vanadium, 0.4 ppm; nickel, 0.15 ppm; copper 0.1 ppm.

Because certain nitrogen compounds are strongly adsorbed on the catalyst, they deactivate it in the same way that coke does (73). Burning of the nitrogen compounds during regeneration restores the activity completely. Basic heterocyclic compounds are particularly bad, whereas ammonia and aliphatic amines have little effect (73,81,82).

Commercially, sulfur poisoning has been experienced principally with natural catalysts with high iron contents (3,82). Hydrogen sulfide and organic sulfur compounds that produce it during cracking cause rapid deterioration of the catalyst, while stable sulfur compounds, like thiophene and its homologs, have little effect. Sulfur poisoning can be alleviated by contacting the catalyst with steam immediately after regeneration or by the use of large amounts of steam elsewhere in the unit (73).

Catalyst Aging. Catalysts lose activity in use, principally because of their exposure to steam at high temperatures (3,73,75), although they deactivate slowly at high temperatures even when steam is absent. Steam is used in catalytic cracking whenever an inert gas is needed, for example, as a sealing gas in moving-bed units and as a stripping medium in all types of units. Steam is also produced in the burning of coke deposits, which contain up to 10 per cent hydrogen. Loss of activity in commercial units appears to be faster than would be predicted from laboratory data, perhaps because catalyst-particle temperatures are higher than the bulk temperatures measured in regenerators (75). Loss of activity on aging is associated with loss of surface area.

Among the natural and synthetic silica-alumina catalysts, resistance to steam deactivation increases with alumina content, and kaolin catalysts have exceptional stability (7). Silica-magnesia catalysts are also quite resistant to steam deactivation (73).

Reaction Conditions

What happens in a moving-bed or fluidized-bed reactor depends upon the temperature, pressure, space velocity, ratio of catalyst to oil passing through the reactor, concentration of coke on the incoming and outgoing catalyst, and catalyst activity. The normal range of each variable is (3,42,46,49*a*,58) given in Table 7-4. Reaction conditions are not independent of each other; changing one of them requires that one or more of the others change (42). Consequently, the relationships among the several variables are too complex to permit their use as primary correlating factors. Consequently, "conversion" is used, and the effects of the various reaction variables are expressed in terms of how they affect yield-conversion relationships.

Table 7-4

	In fluid units	In moving-bed units
Reactor temperature, °F	885–1000	850–925
Reactor pressure, psig	10–16	5–15
Space velocity, w_o/hr ÷ w_c[a]	0.5–3	1–4
Catalyst-oil ratio, weight	5–20	1.5–7
Carbon on regenerated catalyst, wt %	0.3–0.8	0.1
Carbon on spent catalyst, wt %	0.5–2	
Maximum regenerator temperature, °F	1100	1250

[a] $\frac{w_o/\text{hr}}{w_c}$ = weight of oil per hour divided by weight of catalyst in reactor.

Conversion. Conversion is expressed in various ways. Most often, it equals gas-oil disappearance, with gas oil defined as material in the product higher boiling than gasoline; all such material is called catalytic cycle oil. "Corrected conversion" takes into account the presence of gasoline in the charge stock (8). Both of these conversion terms ignore the cracking of heavier gas oils to lighter materials in the gas-oil range. To take this cracking into account, the use of a "20+ conversion" has also been proposed.* If the term is not qualified, the simplest factor (100 minus per cent cycle oil) is generally meant.

In once-through operations, gasoline yields increase with conversion, reach a peak, and then decrease. At the point of maximum gasoline

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* 20+ conversion = 100 − 1.25 (per cent on feed of product boiling above the feed 20 per cent point). Distillation curves of feed and product are determined in a 15:5 distillation, i.e., in a column with 15 or more theoretical plates operated at a 5:1 reflux ratio (8).

yield, the incremental production of gasoline (with increasing conversion) is just balanced by increased cracking of the gasoline product. Higher yields of gasoline are obtained by operating at a lower once-through conversion and recycling the unconverted product (3,22*b*,46). Typical effects of conversion are (46):

Conversion, vol %	35	50	65	75	75 (recycle)
C_5+ gasoline, vol %	29.6	38.6	43.0	43.0	52.6
Coke, wt %	2.1	3.1	6.0	9.8	8.4

Up to conversions of 50 per cent, once-through operations are economical. At higher conversions, recycle operations may be more economical, and recycle is employed generally for conversions above 60 per cent (46). Commercially, conversions have been as high as 92 per cent, with a recycle/fresh feed ratio of 1.34 (49*a*).

The octane quality of the gasoline product improves slightly with increasing conversion, and it is lowered by recycling. In a fluidized-bed operation at 950°F, the effects of conversion on octane quality were (46) as given in Table 7-5.

Table 7-5

Conversion, vol %	Once-through				Recycle
	35	50	65	75	75
Research octane					
Clear	95.5	96.2	96.9	97.5	96.5
Plus 2 cc TEL/gal	99.2	99.8	100.4[a]	100.6[a]	100.0
Motor octane, clear	80.3	81.7	83.0	84.1	81.9

[a] Method of extrapolating above 100-octane rating was not specified.

Temperature. Increasing temperatures increase all the reaction rates, but not in the same proportions. By way of example, the rate of gas-oil disappearance doubles for about 75°F (23*b*), whereas 200°F are required to double the rate of coke production (70). However, for a given conversion in most units, gasoline yields are reduced at higher temperatures (3,5,46,57), presumably because the rates of secondary reactions increase faster with temperature than do the rates of primary reactions. Because a large proportion of a virgin or coker gas oil cracks rapidly, the advantage of low coke yields at high temperatures is said to be obtainable without a loss in gasoline yield by operating at very short contact times (25,51). In such an operation, a second, conventional reaction stage may be employed for cracking the cycle oil from the high-temperature stage (25). The reactor for the first stage is a tall, dilute-phase "riser" reactor, through which the vapor-catalyst mixture passes at high velocities. Cyclones separate the catalyst from the vapors, and the catalyst passes into the second reaction stage.*

In single-stage units, the octane of the gasoline and the unsaturation of the gaseous product increase with increasing temperatures (49,57), as illustrated in Fig. 7-5. Although two-stage units operate with high temperatures in the first stages, they produce gasolines of the same research octane numbers as most single-stage units. The gaseous product from two-stage cracking is more unsaturated (25). Inasmuch as the high unsaturation results from minimizing secondary reactions (including hydrogen transfer), *i*-butane yields are low.

Higher temperatures result in gasolines of slightly higher sulfur contents (76), and the effect is accentuated in a two-stage operation (25).

Pressure. Reaction pressures are usually in the range of 5 to 15 psig. Pressure has little effect on the rate of cracking, although it affects contact time (69). Increasing pressures reduce the unsaturation of the products and the octane quality of the gasoline, and they also increase the production of coke at a given conversion (3).

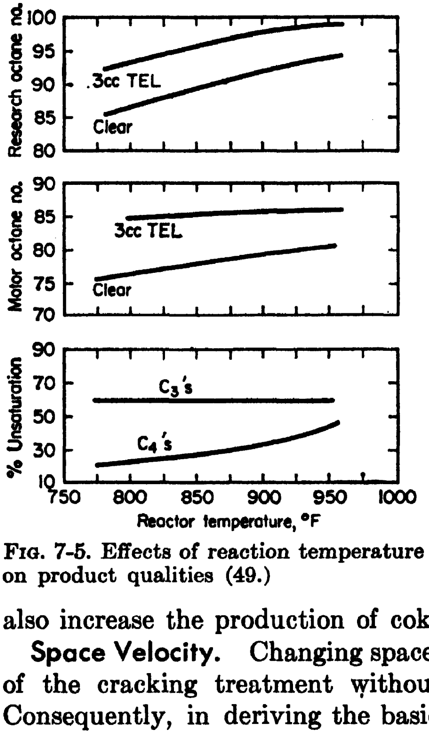

FIG. 7-5. Effects of reaction temperature on product qualities (49.)

Space Velocity. Changing space velocity merely changes the severity of the cracking treatment without changing reaction-rate constants. Consequently, in deriving the basic yield versus conversion curves and the corresponding product-quality curves, conversion is varied by changing the space velocity while holding other variables constant. Thus, by definition of the basic curves, variations in space velocity do not affect product distribution.

Catalyst-to-oil Ratios. Increasing catalyst-to-oil ratios shorten the time required for the catalyst to pass through the reactor and thereby reduce the extent of its deactivation from coke production. Consequently, conversions increase with catalyst-to-oil ratio. At a given conversion and temperature, coke yields are somewhat higher at higher

---

* Two-stage cracking was developed by the Shell Oil Company.

catalyst-to-oil ratios (14,80). However, if the higher ratios are used to raise the temperature of reaction, the effect of the higher temperature may more than counterbalance the catalyst-oil effect, and coke yields may be reduced (14).

Coke Concentrations on Catalyst. The concentrations of coke on the catalyst depend upon how cleanly it is regenerated and on how much coke is deposited per cycle. The effective activity of the catalyst is raised by reducing its average coke level, and somewhat better yields are obtained. However, if lower coke concentrations are obtained by increasing the catalyst-to-oil ratio, this increase may offset the beneficial effects of lower concentrations of coke (80).

In any given unit, the coke on regenerated catalyst goes down as the oxygen content of the flue gas is increased, but coke-burning capacity is reduced. Consequently, there is an optimum residual coke level for each unit. In fluid units, the oxygen content of the flue gas is held at about 1 per cent, and the coke level on regenerated catalyst is in the neighborhood of 0.3 to 0.6 per cent.

On silica-alumina catalysts (including natural catalysts), high coke levels catalyze the production of more coke. If coke levels are allowed to rise much above normal, coke production may "snowball"; when this happens, it is sometimes necessary to cut oil out of the unit while burning the coke off the catalyst (51,61). On silica-magnesia catalysts, coke does not have this catalytic property (15).

Catalyst Activity. As the activity of a catalyst declines, the conversion also declines unless other reaction variables are changed to compensate for the activity change. In any commercial unit, the activity of the catalyst approaches a constant value, which depends on the rate of deactivation and the rate at which fresh catalyst is added. In many units, fresh catalyst is added only to make up for mechanical losses, and the activity of the circulating catalyst drops to 10 to 25 per cent of what it was initially. However, yields are somewhat poorer at low activities (3), and catalyst is sometimes deliberately discarded so that more fresh catalyst can be added to increase activity and thus improve yields. Deliberate discard is also practiced when the cracking capacity of the unit is limited by catalyst activity.

Products

Distinctive features of the products from catalytic cracking are the high octane quality of the gasoline product, the high unsaturation of the C_3 and C_4 cuts, and the high concentration of *i*-butane in the butanes. Other features of some importance are the low sulfur content of the gasoline (relative to the charge stock) and the suitability of the light cycle oil as a component of distillate fuels.

Octane Quality. In moving-bed units, research octane ratings of the clear gasoline range from 86 to 92, motor ratings from 78 to 82 (3). Ratings of gasolines from fluidized-bed units are usually somewhat higher, at least partly because reactor temperatures are usually higher (46). In both types of operation, higher octanes are obtained when synthetic silica-alumina catalysts are used, when naphthenic feeds are charged, and when higher reaction temperatures are employed.

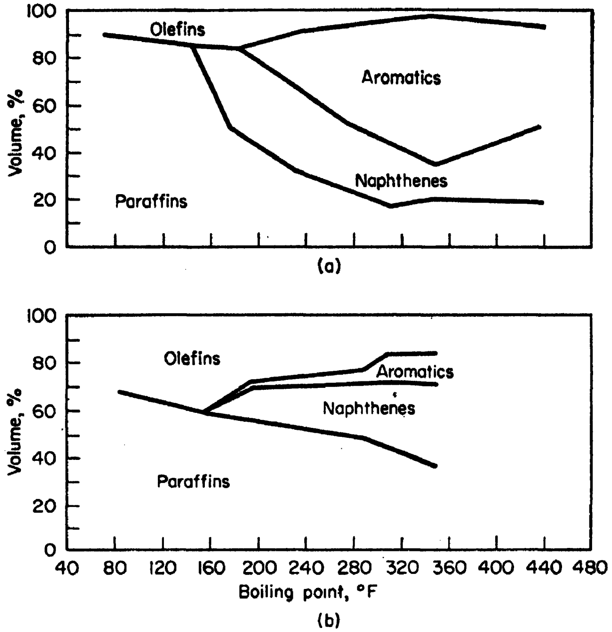

FIG. 7-6. (*a*) Catalytic and (*b*) thermal gasolines made from a light gas oil (3).

Unlike the corresponding fractions of virgin and thermally cracked gasolines, the octane ratings of the lighter and heavier portions of catalytic gasolines are nearly the same. Lighter fractions have high octane numbers because they are rich in *i*-paraffins and olefins; heavier fractions because they are rich in aromatics (3,10). By way of example, the hexane fraction from a catalytic gasoline contained 91 per cent *i*-paraffins; this figure compares with 37 per cent and 49 per cent in hexane fractions from a thermal and a virgin gasoline (3). The aromatic content of the heavy ends may be compared with the corresponding content of a thermal gasoline in Fig. 7-6.

Catalytic gasolines respond well to the addition of tetraethyllead. Typically, the addition of 3 cc per gal increases octane ratings by five to eight units (35,73).

Other Gasoline Qualities. Catalytically cracked gasolines are usually low in corrosive sulfur compounds and in gum-forming constituents; therefore the only treating usually required is a simple caustic wash, followed by the addition of an inhibitor (73).

In most cases, the sulfur concentration in the gasoline is about 10 per cent of the concentration in the fresh feed to cracking, except for feeds from California crudes, which produce higher-sulfur gasolines (73,76). Because the sulfur content of the heavy end of the gasoline is relatively high, the sulfur content of the whole gasoline may be affected markedly by its end point (73). Thiophenes and aromatic thiols are found in gasolines from catalytic cracking, even though they are absent from naturally occurring petroleum oils.

Hydrogenating the pentene fraction from catalytic cracking raises its leaded motor octane rating by as much as 18 units (45), and mild hydrogenation of the fraction boiling above 250°F may be desirable to lessen its tendency to form engine deposits.

Composition of Gases. Except for hydrogen sulfide, the production of which depends upon the sulfur content of the feed, most of the catalytic product lighter than gasoline consists of C_3 and C_4 hydrocarbons, and the unsaturation of these gases varies over a wide range. Probably the major factor in determining unsaturation is the severity of the cracking conditions, inasmuch as hydrogen transfer is a secondary reaction. Thus, low conversions and high-boiling feeds (which crack most easily) favor high unsaturation. High temperatures and low pressures also favor unsaturation.

Light Cycle Oil. The lighter portions of catalytic cycle oils, boiling between 400 and 600°F, are widely used as components of heating oils and diesel fuels (6*a*). For these uses, the quality of a light cycle oil depends upon the feed and the severity of the cracking operation. Higher-quality products are made from lower-boiling feeds, from paraffinic charge stocks, and at lower reaction severities. Relatively low severity can be achieved in a high-conversion unit by recycling only the heavy catalytic cycle oil. Low temperatures and high oil partial pressures are also favorable to light-cycle-oil quality. Sulfur content is usually about 85 per cent of the sulfur content of the feed (6*a*).

The stabilities of catalytic cycle oils are usually satisfactory if they are caustic-washed as they are taken off the unit and before they contact air (9*a*).

The quality of a light cycle oil can be improved by hydrogenation (20,44) or by solvent extraction (12,63).

Feed Stocks

Feed stocks to catalytic cracking range from light gas oils, somewhat heavier than kerosene, to reduced crudes. Their performance depends upon boiling range, distribution of hydrocarbon types, the concentrations of sulfur and nitrogen, and the presence, or absence, of Conradson carbon

Table 7-6. Representative Yields in Fluid Catalytic Cracking (56)

	Virgin gas oils				Wax	Deas-phalted oil	Catalytic cycle oils						Motor-oil extracts		A[a]	B[b]	C[c]
Gravity, °API	39.4	29.3	28.0	24.5	35.3	21.4	22.5	29.0	22.5	29.5	28.7	31.0	18.0	12.9	30.4	17.9	19.8
IBP at °F	468	531	530	390	612	552	530	560	558	440	481	445	610	399	386	478	474
10% at °F	513	595	610	636	666	661	598	612	601	486	489	454	656	.....	439	557	514
30% at °F	538	674	651	.....	696	.....	644	640	625	506	535	456	.....	.....	466	666	617
50% at °F	551	.....	685	.....	.....	.....	677	657	642	524	550	459	.....	.....	493	.....	700
70% at °F	568	.....	.....	.....	.....	.....	.....	678	661	552	568	463	.....	.....	541		
90% at °F	604	.....	.....	.....	.....	.....	.....	.....	686	607	595	471	.....	.....	653		
EP at °F	680	.....	.....	.....	.....	.....	.....	.....	.....	688	635	523					
Per cent at 700°F	....	48	59	23	33	21	65	85	95	.....	.....	.....	25	8	95	42	50
Conradson carbon residue, wt %	0.0	0.0	0.0	0.2	.....	3.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	2.5	0.0	3.5	3.3
Sulfur, wt %	0.3	0.3	0.2	0.4	.....	0.5	0.9	0.6	0.7	0.4	0.4	0.6	0.5	0.8	0.4	0.7	0.6
Aniline point, °F	166	222	183	219	.....	209	156	171	160	127	137	88	150	185	122	148	142
Diesel index	59.6	65.0	50.5	53.7	.....	44.7	35.1	49.6	36.0	37.5	39.3	27.4	27.0	20.4	37.1	26.5	28.1
A. Severity 1																	
Coke, wt %	1.6	3.0	3.2	7.0	2.5	6.0	4.5	3.7	3.3	2.4	1.9	1.3	5.5	10.0	3.9	8.5	9.0
Dry gas, wt %	4.5	6.2	5.9	11.1	9.8	5.6	5.1	5.1	3.7	4.8	4.2	3.4	5.6	5.8	4.7	5.8	4.0
Propene, vol %	3.3	5.2	4.8	4.6	10.2	3.5	3.2	3.2	2.4	3.8	3.4	2.7	1.7	3.0	3.9	4.2	3.4
Total C_4's, vol %	8.2	12.1	10.9	9.7	22.0	7.6	9.6	10.0	7.2	8.4	7.4	6.8	9.3	8.9	7.2	6.8	6.9
C_5+ gasoline, vol %	25.6	46.0	34.1	54.0	52.0	47.8	27.4	27.4	20.0	22.5	21.0	22.6	36.9	41.0	23.0	27.4	26.0
Light cycle stock, vol %	64.0	17.0	33.1	19.0	8.0	21.4	30.6	30.6	34.0	68.0	71.0	71.0	23.0	17.0	55.0	29.0	32.0
Heavy cycle stock, vol %	1.0	24.0	18.9	14.0	17.0	19.6	31.4	31.4	37.0	0	0	0	28.0	26.0	9.0	31.0	30.0
B. Severity 2																	
Coke, wt %	0.8	2.0	1.8	5.0	1.8	4.9	2.9	2.1	2.6	1.1	0.9	0.6	2.7	7.8	1.9	6.0	5.8
Dry gas, wt %	2.7	4.7	4.4	5.4	9.1	4.3	3.4	3.4	2.1	2.8	2.3	2.0	3.8	4.0	2.7	3.8	2.5
Propene, vol %	2.1	3.9	3.0	3.9	9.5	2.8	2.2	2.2	1.4	2.2	1.8	1.4	1.5	2.0	2.4	2.6	2.0
Total C_4's, vol %	4.9	8.8	7.5	7.0	20.6	5.3	6.2	6.6	3.9	5.0	4.1	2.6	5.6	7.1	4.6	5.2	3.2
C_5+ gasoline, vol %	20.0	39.0	29.0	49.0	50.0	41.7	21.1	21.1	12.7	15.5	13.4	16.1	31.0	35.0	16.5	23.0	21.0
Light cycle stock, vol %	73.4	20.0	37.9	23.0	9.0	23.7	34.8	34.8	38.0	79.0	82.0	82.0	25.0	20.0	65.0	30.0	37.0
Heavy cycle stock, vol %	2.6	32.0	25.1	19.0	26.0	28.3	38.2	38.2	44.0	0	0	0	37.0	34.0	10.0	36.0	36.0

[a] Feed A is gas oil obtained by visbreaking a Duo-Sol extract from a crude residuum.

[b] Feed B was obtained by propane-deasphalting feed A.

[c] Feed C was obtained by propane-deasphalting the tar from the visbreaking operation.

and metallic constituents. Yields from the fluidized-bed cracking of 17 representative feeds are given in Table 7-6.

Boiling Range. At constant conversion, gasoline and coke yields increase with boiling range, whereas the yields of dry gas, butanes, and butenes decrease. In fluidized-bed cracking, yields from three feeds from the same crude at 60 per cent conversion were (46) as given in Table 7-7. The adjusted coke yields were obtained by subtracting out the Conradson carbon, which often deposits completely as coke (29,55). These results suggest that the true catalytic coke may be less for higher-boiling materials at a given conversion. In a moving-bed unit, the yield of debutanized gasoline was little affected by feed boiling range at constant coke yield, but conversions were lower for the higher-boiling feeds (3).

Table 7-7

Inspections and yields	Light gas oil	Heavy gas oil[a]	Vacuum gas oil
50% point (TBP), °F	536	781	900
Conradson carbon, wt %	0.06	0.28	2.6
Gasoline (10 lb RVP), vol %	37	45	49
Coke, wt %	3.5	3.7	5.2
Adjusted coke, wt %	3.4	3.4	2.6

[a] Yields adjusted to 60 per cent conversion.

Virgin gasolines do not crack much under ordinary cracking conditions, although they are desulfurized (24) and their octane ratings may be improved by 5 to 20 units (6*a*,58). In most cases, it is desirable to exclude naphthas from the feeds, because economics favor charging gasoline to catalytic reforming. The octane rating of a catalytically cracked gasoline is lowered if the initial boiling point (ASTM distillation) of the feed drops below 475°F (61).

Composition. The chemical composition of the feed affects the yields from catalytic cracking. As shown in Fig. 7-7, the more naphthenic the feed, the higher is the yield of gasoline. Gasoline yields can be predicted approximately if the percentages of paraffinic, aromatic, and naphthenic carbons in the feed are known (82).

Inasmuch as the more susceptible materials crack first, cycle stocks from catalytic cracking are poorer charge stocks than the original feeds. The higher the conversion in the first-pass operation, the poorer is the resulting cycle stock.

Conradson Carbon and Metals For heavy feeds, cracking values depend in large measure on how "clean" they are. High-boiling stocks

—particularly residuums—may contain appreciable quantities of Conradson carbon and metals. Inasmuch as Conradson carbon deposits preferentially on the catalysts (29,55), a high carbon content reduces the capacity of those units that are limited by regeneration capacity. Metals also deposit on the catalyst and change its selectivity in the direction of less gasoline and more coke. To counteract this effect, a portion of the circulating catalyst is sometimes discarded and replaced by fresh catalyst (22*a*). Retentions of metals in fluidized catalysts have been reported at 50 per cent and at 95 per cent (17,28). For moving-bed operations it is stated that "poisoning becomes evident when the metals content on the equilibrium catalyst exceeds 60 ppm of nickel or 400 ppm of vanadium" (6*a*).

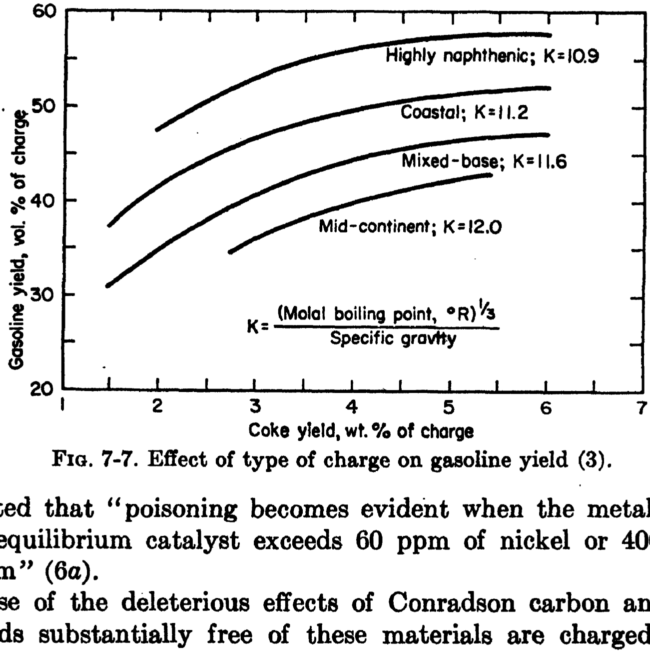

FIG. 7-7. Effect of type of charge on gasoline yield (3).

Because of the deleterious effects of Conradson carbon and metals, only feeds substantially free of these materials are charged to most cracking operations. However, the processing of residuums in moving-bed Houdresid units is being promoted (16). In this process, the effects of metals are minimized by the use of large-size catalysts. Metals concentrate near the external surface, and they are eliminated from the unit as the surface is worn off (38). High coke yields are less deleterious, of course, in a unit designed to handle them.

Arguments have also been advanced (62) to show that the processing of higher-carbon and higher-metals stocks would be economical in fluidized beds, also, if units were designed for such stocks. Reduced crudes have been cracked in experimental fluid units (29).

Preparation of Feed Stocks

In the preparation of feed stocks for catalytic cracking, there are two principal objectives: to eliminate Conradson carbon and metals from reduced crudes while minimizing the rejection of good charge stock, and to eliminate other undesirable materials from virgin gas oils and cycle oils. For the elimination of Conradson carbon and metals, vacuum distillation, deasphalting, visbreaking, and coking have been used. Hydrogenation (37,48,77) and a treatment with BF_3 ether (62) have also been proposed. All these operations are applied to recover charge stock from the bottoms from a crude-distillation unit.

For the removal of other undesirable materials from virgin gas oils and cycle oils, solvent extraction and hydrogenation are employed to a limited extent.

Vacuum Distillation. In petroleum distillation operations, pressures as low as 40 mm of mercury (absolute) are used commercially. At such pressures, substantial quantities of high-quality feeds are recoverable from atmospheric residuums. In one such installation, 40 to 45 per cent of a reduced crude is recovered with a metals content less than 0.1 ppm, in a unit that operates at a furnace outlet temperature of 775°F and a flash-zone pressure of 75 mm Hg absolute (2).

Vacuum distillation is limited by the fact that some of the Conradson-carbon and metal-bearing components are volatile (28).

Deasphalting. Deasphalting consists of precipitating asphaltic materials from residuums, particularly from vacuum residuums (31). Because aromatics are rejected preferentially, paraffinic feed stocks for catalytic cracking can be recovered from even the heaviest feed stocks. When used for this purpose, the operation is sometimes called "solvent decarbonizing." Propane is usually used as the precipitant (32,50,54), although butane can also be used (28,31).

Heavy ends are rejected from a reduced crude by contacting it with propane at the proper temperature. The operation is carried out at 140 to 190°F, at pressures of 450 to 600 psi, and at propane:feed ratios of about five volumes per volume. Deasphalting operations are discussed in Chap. 11, and some typical results are shown in Table 7-8.

Deasphalting may be considered as an alternate to vacuum distillation. At the same yield of gas oil, the deasphalted product is a better cracking feed than a vacuum distillate made from the same reduced crude (28). However, from an economic standpoint, the best use of deasphalting is said to be after vacuum distillation to the point where undesirable materials begin to rise sharply in the distillate (31). The Conradson carbon that remains in a deasphalted gas oil is not necessarily undesirable; it may give reasonable yields in cracking (31).

Coking. Coking (discussed in Chap. 6) is also practiced on atmospheric and on vacuum residuums. The products consist of gas, gasoline, gas oil, and coke. In most cases, conditions favoring maximum yields of gas oil are preferable, because higher yields of a higher-quality gasoline can be realized from catalytically cracking gas oils than can be obtained in the thermal production of gasoline in the coking operation.

When practiced commercially on atmospheric residuums and similar stocks, coking inherently includes distillation of lighter hydrocarbons from heavier hydrocarbons. In such cases, the gas-oil product includes some virgin gas oil.

Deep reduction of the charge stock prior to coking is desirable, because, otherwise, some of the virgin gas oil is cracked thermally in passing through the coking unit. In each particular case, of course, an economic balance must be made to determine how the improved product quality compares economically with the increased costs associated with deep reduction.

Table 7-8. Typical Deasphalting Operations (28,31)

	Reduced crude							
	Texas	West Texas		Middle East		California	Canadian	West Kansas
Charge:								
Vol % on crude	11.1	19.8	29.2	22.2	32.3	20.0	16.0	15.0
Gravity, °API	11.3	13.0	12.0	5.3	10.1	6.3	9.6	10.3
Conradson carbon, wt %	15.0	13.3	12.1	21.5	16.0	22.2	18.9	7.5
Metals,[a] ppm	56	96	58	129	89	369	117	288
Deasphalted oil:								
Vol % on charge	62.9	69.0	66.0	35.0	47.0	52.8	67.8	51.2
Gravity, °API	19.0	20.5	19.6	19.3	20.3	18.3	17.8	18.2
Conradson carbon, wt %	4.2	2.6	2.2	4.3	2.6	5.3	5.4	4.2
Metals,[a] ppm	2.8	1.8	3.1	3.8	2.9	13.9	5.3	17.6

[a] Mostly nickel, vanadium, and iron.

Visbreaking. Visbreaking (also discussed in Chap. 6) is sometimes used to produce gas oil from crude residuums, and sometimes the visbroken oil is vacuum-flashed to maximize the yield of gas oil. Gas-oil yield is lower than obtained from coking.

Pretreatment with Boron-Fluoride-Ether. Pretreatment of reduced crudes with a small amount of BF_3 ether complex, for example, 2.5 vol per cent, has been proposed to make reduced crudes suitable as charge stocks to catalytic cracking. The pretreatment breaks down protective colloids that hold asphaltenes in suspension, and they are drawn off with the reagent. Considerable proportions of the Conradson carbon and of the metals are left behind by the treatment, but it is argued that further elimination of these constituents is uneconomical (62).

Solvent Extraction and Adsorption. Solvent extraction is used to a limited extent to improve fresh feeds (23*a*) and cycle oils (12,74) as charge stocks to catalytic cracking, and adsorption has been proposed (71). From both types of feeds, both operations remove refractory compounds that yield relatively little gasoline in catalytic cracking, but produce relatively large amounts of coke. Solvent extraction also removes sulfur compounds, particularly if hydrogen fluoride is used as the solvent. Typical improvements in cracking yields achieved via solvent extraction of cycle oils are indicated in Table 7-9. Solvent-extraction and adsorption operations are discussed in Chap. 4.

Table 7-9. Effects of Solvent Extraction on Cracking Qualities of a Cycle Oil (74)

	Catalytic cycle oil				
	Total	Raffinate			Extract
Vol % of feed:	100	75	66	60	34
Gravity, °API	18.2	....	.....	....	−0.5
Sulfur, wt %	1.14	0.9	0.45	0.2	
Conradson carbon, wt %	2.0	0.7	0.15	0.0	
Conversion, vol %	25.2	29.9	43.0	52.9	22.6
Cracking yields:[a]					
C_5+ gasoline, vol %	16.8	20.1	33.6	42.2	3.0
Carbon, wt %	5.7	4.7	2.3	1.6	12.0

[a] On charge to cracking.

Hydrogenation. Like extraction and adsorption, hydrogenation improves a feed to cracking by reducing the concentrations of polycyclic aromatics and sulfur compounds; the nitrogen content and Conradson carbon are also reduced. Unlike extraction and adsorption, hydrogenation involves no volume loss, because the undesirable materials are converted to more desirable hydrocarbons (27,37,64,83,84). Illustrations of the effects of hydrogenation are given in Table 7-10, and the operations are discussed in Chap. 12.

Some gasoline is produced in the hydrogenation of feeds to catalytic cracking. Gasolines produced from virgin or coker gas oils have low octane ratings and would have to be upgraded. Gasolines produced from cycle oils have high octane ratings.

Design Considerations

The design of catalytic cracking units involves the problems inherent in any moving-bed or fluidized-bed system; these were discussed in Chap. 5. Other problems of concern in catalytic cracking are afterburning, the recovery of heat from flue gases, and the fouling of preheat equipment.

Table 7-10. Effects of Hydrogenation on the Cracking Qualities of Gas Oils

	Virgin (33)		Virgin (19)		Virgin (19)		Virgin (64)		Heavy virgin (27)		Heavy catalytic cycle (37)		Heavy catalytic cycle (26)		Coker (27)		Visbreaker (19)	
	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
Hydrogen consumption, scf/bbl	...		300		110		400		675		...		...		625		220	
Hydrogenation yields, vol %:																		
Gasoline	.....	.....	.....	5.5	.....	0.0	0	9.5	3.5	15	0	0.3	0	4.9	8.5	19.0	.....	0.0
Gas oil	.....	.....	100	96.4	100	100.5	100.0	92.0	96.5	87	100.0	101.0	100.0	98.8	91.5	82.0	100.0	100.0
Gas-oil properties:																		
Gravity, °API	22.3	26.2	24.8	30.2	29.8	31.9	27.5	32.0	21.2	27.9	19.3	23.4	26.5	32.1	25.1	31.6	24.6	27.2
Sulfur, wt %	2.11	0.22	2.66	0.24	0.51	0.06	1.8	<0.1	1.18	0.06	2.25	0.40	0.47	0.07	2.42	0.09	0.72	0.16
Nitrogen, wt %	0.20	0.15	0.09	0.04	0.08	0.04	.....	.....	0.37	0.06	.....	.....	.....	.....	0.32	0.09	0.16	0.16
50% boiling point, °F	.....	.....	741	682	751	725	.....	.....	720	680	650	630	644	624	590	565	940	911
Cracking yields (on feed to cracking):																		
Coke, wt %	3.2	3.2	4.9	3.4	6.2	4.6	6.0	3.8	10.0	6.5	6.6	6.6	6.7	2.1	6.5	4.6	3.2	2.3
C_5+ gasoline, vol %	38.5	41.1	37.5	37.7	39.7	40.7	43.0	45.5	35.0	38.5	18.3	26.0	28.7	36.4	27.4	28.1	40.4	40.9
Cycle oil, vol %	48.0	44.1	50.0	50.0	50.0	50.0	40.0	40.0	40.0	40.0	69.0	56.4	52.2	51.5	48.1	48.6	50.0	50.0
Gasoline from cracking:																		
Research octane no. (3cc TEL)	97.0	98.9	94.8	96.4	96.2	96.3	97.0	99.5	97.5	99.5	95.6	101.0	.....	.....	98.0	99.7	94.8	94.8
Motor octane no. (3cc TEL)	82.6	86.1	.....	.....	.....	.....	.....	.....	.....	.....	82.6	86.0						
Sulfur, wt %	0.27	0.04	0.29	0.03	.....	.....	0.15	<0.01	0.3	<0.01	0.14	0.02	.....	.....	.....	.....	0.10	0.02
Cycle oil:																		
Gravity, °API	.....	.....	23	28	28.5	30	22.0	27.0	16.5	23	.....	.....	22.1	27.5	19.8	27.4	23	25
Sulfur, wt %	.....	.....	2.3	0.25	.....	.....	1.5	0.1	0.8	0.01	.....	.....	.....	.....	2.10	0.08		

Afterburning. Afterburning is a problem in catalytic cracking units because the flue gas contains both CO and O_2. Sometimes the CO burns to CO_2 in the space above the normal catalyst level (53). In the presence of appreciable concentrations of catalyst, little damage results. However, where little catalyst is present to absorb the combustion heat, destructively high temperatures may occur. To avoid such occurrences, water and/or steam nozzles are provided at critical points to quench any incipient afterburning (1,39,59,66). Quench nozzles are particularly desirable in effluents from primary cyclones of fluidized-bed units, in which catalyst concentrations are low. Because hot metallic surfaces are believed to catalyze afterburning, cyclones are often lined with ceramic materials; the lining also minimizes wear (61). The probability of afterburning increases as temperature is increased, especially above 1100°F.

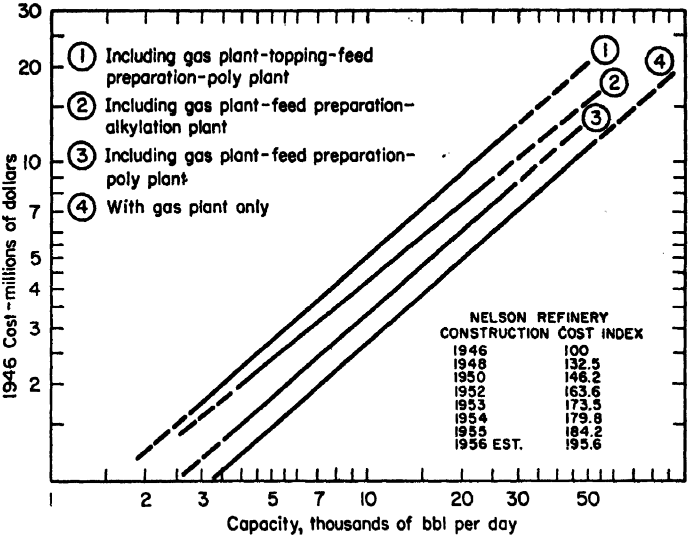

FIG. 7-8. Investment costs for catalytic-cracking units (47).

Recovery of Heat from Flue Gases. Because flue gases from catalytic cracking units contain large quantities of CO, a considerable amount of energy is recoverable from them, and CO boilers have proved economic in some cases (11,18).

Fouling of Preheat Equipment. The fouling of preheat equipment is frequently a troublesome problem. Oxygen in the feed is believed to be the principal cause. Normally, little trouble is experienced if the feed is taken directly off a fractionation unit as a distillate. If the feed is sent to intermediate storage, gas blanketing the storage, stripping the charge with natural gas, and periodic injection of steam into the exchangers help to alleviate fouling (59,60).

Investment and Operating Costs

Little has been published on the investment and operating costs for catalytic cracking. Some typical investment costs are shown in Fig. 7-8. Because investment costs vary with location and with the process and mechanical standards of the purchaser, large variations from these costs are possible. Investment costs for vacuum flashing for feed preparation were estimated at $26 to $50 per bbl of feed in 1956 (47).

In 1957, operating costs were indicated (47) to be 28 to 50 cents per bbl of feed for catalytic cracking (exclusive of royalty charges of about 5 cents per bbl), and 7.5 to 18 cents per bbl of feed for vacuum flashing. Steam consumption in catalytic cracking was stated to be 17 lb per bbl of feed. Catalyst usage is an appreciable item; it may range from 0.1 to 1 lb per bbl of charge.

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CHAPTER 8

CATALYTIC REFORMING

Because higher-octane gasolines permit the building of engines that extract more power from gasoline, there has been a constant push toward higher octanes since differences in octane quality were first recognized. A major factor in this development has been the large-scale use of catalytic reforming to raise octane ratings of gasoline stocks. The first commercial unit, a Hydroformer, went on stream just before World War II, and the process proved to be a major source of aromatics and aviation gasoline for military uses (55). However, catalytic reforming did not "catch on" until about 1950, when Haensel and others at the Universal Oil Products Co. demonstrated that platinum catalysts* could be used commercially despite their high costs.† By 1955, catalytic reforming processes had almost completely supplanted thermal reforming. Catalytic processes not only give higher-quality products, they give higher yields as well (24,32).

Reactions

In catalytic reforming, the principal object is to convert other hydrocarbons to aromatics. The reason may be seen by comparing the octane numbers of some corresponding hydrocarbons (Table 8-1). Thus, high

Table 8-1

	Research rating	Motor rating
n-Heptane	0	0
2-Methylhexane	42	45
Heptene-2	73	57
Methylcyclohexane	75	71
2-3-Dimethylpentane	91	89
2-2-3-Trimethylbutane (triptane)	113	101
Toluene	120	104

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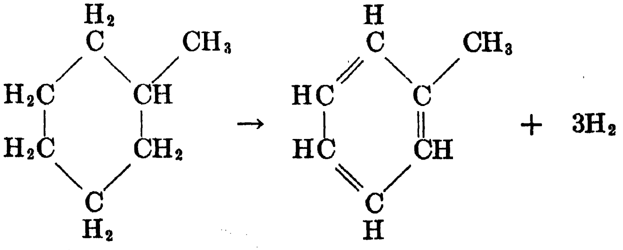
* The activity of platinum catalysts for promoting dehydrogenation reactions was discovered in 1911 by N. D. Zelinsky in Russia (57).

† Although platinum has fluctuated between $85 and $115 per troy ounce, the platinum inventory of a large unit is measured in tons.

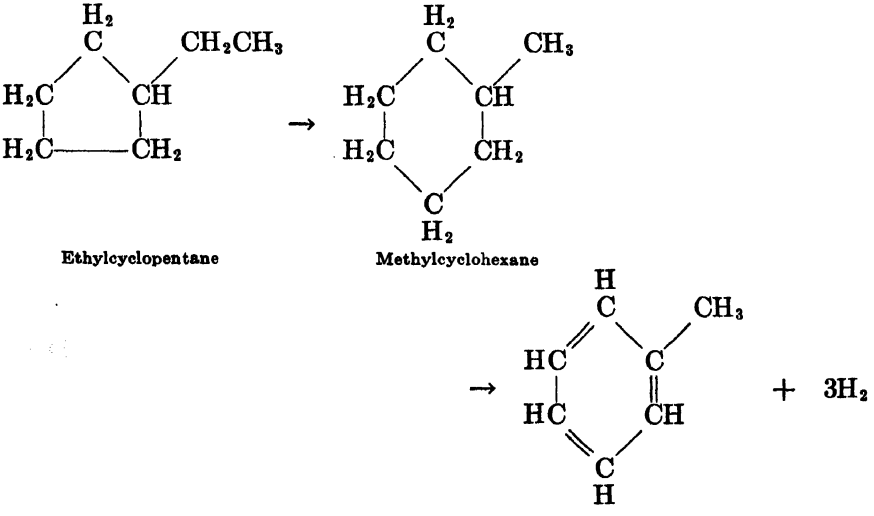
conversions to aromatics result in high-octane products. There is a loss in volume, because aromatics are denser than other hydrocarbons; however, the loss is small in comparison with the loss (to gas and tar) suffered in thermal reforming. How the composition of a catalytic reformate compares with the composition of a thermal product is shown in Fig. 8-1. Other reactions of some importance in catalytic reforming are cracking and isomerization.

Production of Aromatics. Because aromatics contain less hydrogen than do other hydrocarbons, dehydrogenation is the primary reaction. Of the nonaromatics, cyclohexane derivatives are dehydrogenated most readily:



Methylcyclohexane Toluene

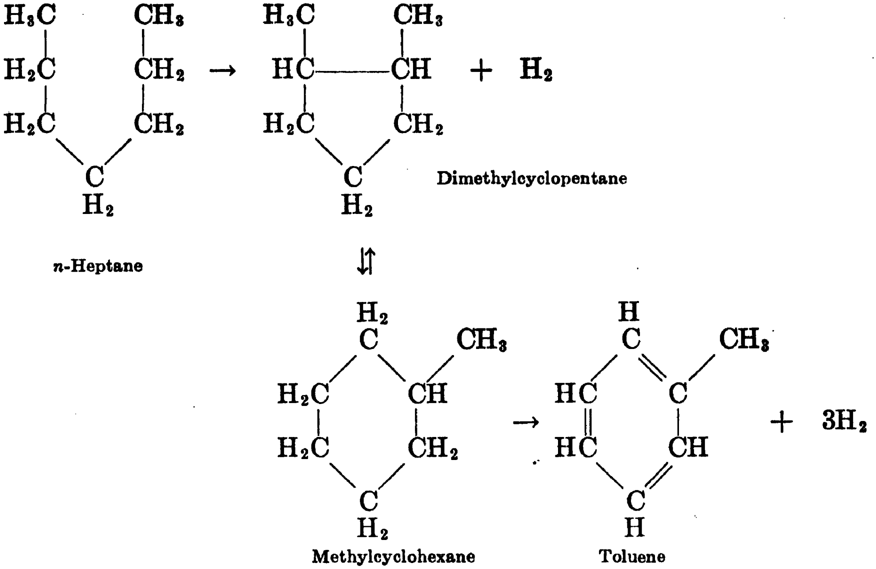
Cyclopentane derivatives react similarly, but they require a preliminary isomerization to cyclohexane derivatives:



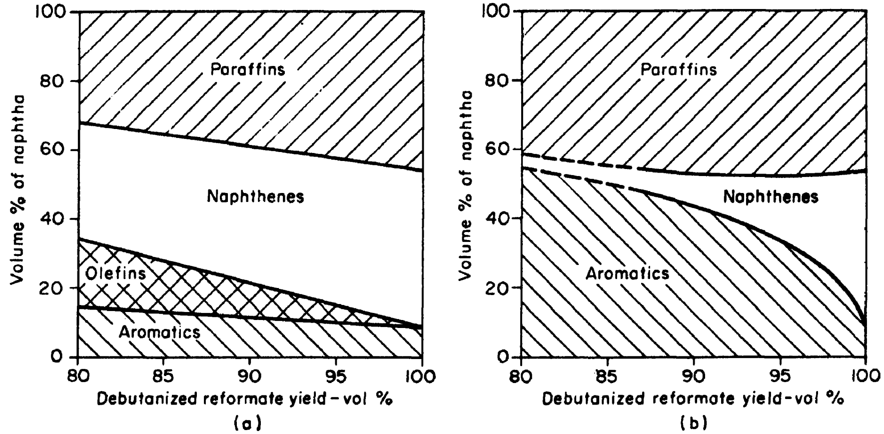
Ethylcyclopentane Methylcyclohexane

Toluene

Conversion of paraffins to aromatics involves a cyclization step. For normal heptane, the reactions may be written:



To undergo these reactions, a paraffin must have at least six carbon atoms in a chain or be isomerizable to such a compound.



(a)

(b)

FIG. 8-1. Comparison of products (a) from thermal reforming and (b) from mild catalytic reforming (19).

Aliphatic olefins can also be converted to aromatics directly, but this fact is of little practical significance because such olefins are readily hydrogenated to paraffins under the conditions used in catalytic reforming. Thus, aliphatic olefins behave as paraffins, with the exception that they deactivate the catalyst more rapidly (9a). Similarly, cyclic olefins behave as naphthenes.

Hydrocracking. Under the conditions employed in catalytic reforming, cracking competes with dehydrogenation reactions. Because high hydrogen pressures are used, any olefins that form are saturated immediately, and the reactions are usually called "hydrocracking." Whether hydrocracking occurs in one step or in two is of little consequence. In either case, a typical over-all reaction is:

$$\underset{\text{Octane}}{CH_3(CH_2)_6CH_3} + H_2 \rightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + \underset{\text{Pentane}}{CH_3(CH_2)_3CH_3}$$

Because lower-boiling paraffins have higher octane numbers, hydrocracking improves octane ratings; however, the improvement is less than if the paraffins were converted to aromatics. Also, there is considerable loss of gasoline to butanes and lighter materials, and the vapor pressure of the debutanized product is raised. Increasing the vapor pressure reduces the amount of butane that can be blended into the product to make a finished gasoline; thus, the effective yield of gasoline is reduced still further.

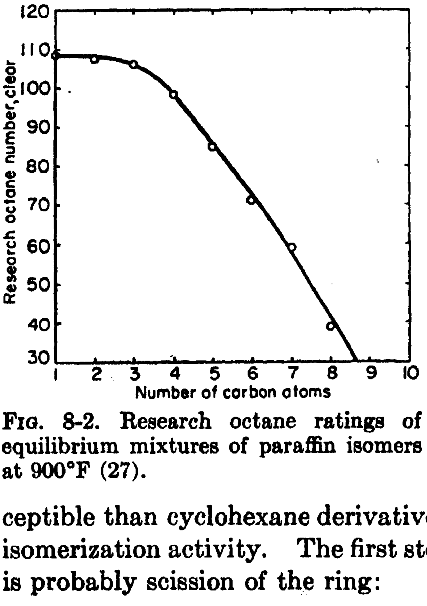
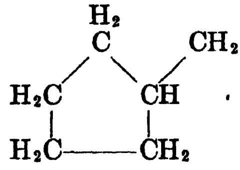


FIG. 8-2. Research octane ratings of equilibrium mixtures of paraffin isomers at 900°F (27).

Hydrocracking of naphthenes also occurs to some extent. Cyclopentane derivatives are more susceptible than cyclohexane derivatives, especially over catalysts with little isomerization activity. The first step in the hydrocracking of naphthenes is probably scission of the ring:



$+ H_2 \rightarrow CH_3(CH_2)_5CH_3$

Ethylcyclopentane Hydrogen Heptane

The paraffin so formed may react further to produce aromatics, or it may be hydrocracked.

Isomerization. With some catalysts, paraffins are isomerized under reforming conditions. Usually, isomerization of paraffins does not have a large effect on octane quality because the productions of highly branched paraffins are small (17,21,25,27). The octane numbers of equilibrium mixtures of paraffins at reforming temperatures are shown in Fig. 8-2. If the paraffins in a given charge were chiefly normal, their isomerization would have a large effect on octane (20). In most instances, however, paraffins in the charge are mixtures of isomers; therefore the isomerizing activity of a catalyst is important chiefly for the isomerization of cyclopentane derivatives.

Catalysts

Although aromatics can be produced from other hydrocarbons without catalysts, severe conditions are required, and yields are low. To obtain acceptable yields, dehydrogenation catalysts must be employed. Those of commercial interest include platinum on alumina, platinum on silica-alumina, chromia on alumina, molybdena on alumina, and cobalt molybdate on alumina.* The approximate compositions of these catalysts are given in Table 8-2.

Table 8-2. Compositions of Reforming Catalysts

Catalyst base	Dehydrogenating element	Per cent	Other elements	Per cent
Alumina.............	Molybdena	10–15		
Alumina.............	Platinum	0.3–0.6	Halides	0–1
Alumina.............	Chromia	10–15		
Alumina.............	Cobalt molybdate			
Silica-alumina........	Platinum	<1.0		

The ideal catalyst would convert all other hydrocarbons selectively to aromatics rapidly, with only a small catalyst inventory. Such a catalyst would not promote hydrocracking, and it would have to operate under conditions thermodynamically favorable to the production of aromatics. To the extent that a catalyst deviates from these conditions it is a poorer catalyst.† Deviations may be either in the selectivity of the catalyst

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* Bauxite is also used for "catalytic reforming" (4,14). However, the operation appears to be little different from thermal reforming at low pressures.

† If the catalyst must operate under conditions such that equilibrium considerations limit the production of aromatics, then hydrocracking activity may be desirable to obtain additional octane improvement. In the few refineries that have a deficiency of butanes, hydrocracking may be desirable, at least at lower-octane levels. A paper comparison of hydrocracking and isomerization against dehydrocyclization for a hexane-through-nonane feed indicated higher yields of butane and heavier for the hydrocracking route (18). However, the hydrocracked product would have a large butane content, the dehydrocyclization product none. If compared at the same vapor pressure (the pertinent comparison in most cases), the yield by way of dehydrocyclization should be the larger. Further, it was assumed for the paper comparison that the hydrocracked product would have the equilibrium distribution of isomers, whereas actual products are deficient in the high-octane multibranched isomers (27). Finally, the feed stock included 20 per cent of a six-carbon-atom fraction, which would usually be excluded from a reformer feed.

toward the production of aromatics or in the activity of the catalyst for the several reactions that actually occur. Selectivity is determined by the relative rates of the competing reactions—dehydrogenation to aromatics and hydrocracking, and isomerization in so far as it affects the other two. Activity is determined by the magnitude of the rate constants. Platinum catalysts appear to be the most selective and the most active, as well as the most expensive.

Dehydrogenation of Naphthenes. Selectivities of catalysts depend to some extent on the make-up of the feed stock. Alkylcyclohexanes are readily converted to aromatics by all dehydrogenation catalysts, provided that the reaction conditions are favorable thermodynamically. For the conversion of alkylcyclopentanes, on the other hand, there are large differences. Because alkylcyclopentanes require an isomerization step, their conversion to aromatics depends upon the isomerization activity of the catalyst. Published data (20,27) on platinum, molybdena, and chromia catalysts show that platinum has the highest isomerization activity, chromia the lowest. Even with platinum catalysts, the isomerization reaction is the rate-controlling step (27). Thus the conversion of alkylcyclopentanes to aromatics is slower than the conversion of cyclohexane derivatives; consequently there is more opportunity for hydrocracking, and yields of aromatics are poorer (18).

Dehydrocyclization of Paraffins. Data on platinum, molybdena, and chromia catalysts have also been published for the conversion of paraffins to aromatics (13,20,27). When operating in the pressure range normally used in catalytic reforming, platinum is the most effective catalyst, chromia the least. The poor results obtained with chromia catalyst are surprising, inasmuch as high conversions of *n*-heptane to toluene are obtained at low pressures (20). Apparently, the chromia catalyst has the unusual property of adsorbing hydrogen so strongly at higher pressures that paraffins cannot readily reach its surface.

Reaction Mechanism

Extensive studies have been made to elucidate the mechanism of reforming over platinum catalysts (10,35*a*,65). Such catalysts are dual-functional (35*a*); they contain platinum as a dehydrogenating agent and an acidic material, such as chlorine, fluorine, or alumina-promoted silica, as an isomerization agent. In commercial catalysts, enough platinum is used to ensure that the dehydrogenation activity is large in comparison with the isomerization activity (65).

Although only traces of olefins can exist under reforming conditions, they apparently are intermediates in the reactions (10,35*a*). Both naphthenes and paraffins are dehydrogenated to olefins (in trace amounts) on dehydrogenation sites in the catalyst. Cyclohexenes continue to dehydrogenate rapidly to aromatics. Alkylcyclopentenes transfer to acid sites, where they are isomerized to cyclohexenes; the cyclohexenes then pass back to dehydrogenation sites, where they are converted to aromatics. Alkyl olefins also transfer to acid sites where they may either isomerize to other alkyl structures or cyclize to naphthenes. The isomerized olefins pass back to dehydrogenation sites, where alkyl olefins are hydrogenated to paraffins and cyclohexenes are dehydrogenated to aromatics.

In view of the low isomerization activity of chromia catalysts, the excellent results obtained with them at low pressure suggest that *n*-heptane is easier to aromatize than are its isomers. This idea is also suggested by data on the conversion of *n*-heptane over a platinum catalyst (27); the ratio of aromatics production to hydrocracking was higher at low conversions (where *n*-heptane predominates in the reactants) than at higher conversions (where *i*-heptanes predominate). It has also been shown that paraffins with more than seven carbon atoms are converted more readily to aromatics than are heptanes (27). All these observations fit the hypothesis that naphthene intermediates are not formed from paraffins over platinum catalysts by the linking of two end (primary) carbon atoms. It has been suggested (27) that platinum catalysts form derivatives of cyclopentane by the linkage of second and sixth carbon atoms; the alkylcyclopentanes so formed isomerize to alkylcyclohexanes, which are dehydrogenated to aromatics. This mechanism could not apply for chromia catalysts, which have little isomerization activity. When *n*-heptane is processed over a chromia catalyst, the second and seventh carbon atoms appear to link up to form methylcyclohexane directly.

Reaction Conditions

Catalytic reforming is carried out over a wide range of reaction conditions, the most important of which is pressure. Other variables include recycle gas rate, temperature, space velocity,* and the particle size of the catalyst.

Reaction Variables. Thermodynamically, dehydrogenation is favored by low pressures and high temperatures. However, these conditions also favor the formation of a carbonaceous deposit ("coke") that deactivates the catalyst. Fortunately, the deposition of coke can be suppressed by operating in an atmosphere of hydrogen; the higher the pressure of hydrogen, the slower the deposition (69). Also, increasing the pressure of hydrogen does not severely retard the dehydrogenation

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* Space velocity is the ratio of oil charge rate to catalyst inventory in the on-stream reactors, expressed as weight per hour per weight (wt/hr/wt) or as volume per hour per volume (vol/hr/vol).

reactions that produce aromatics. Consequently, catalytic reforming is carried out under substantial pressures, with the hydrogen product recycled to the reaction zone.

How the equilibriums are affected by pressure and by the recycle of hydrogen is shown in Fig. 8-3 for methylcyclohexane-toluene and in Fig. 8-4 for *n*-heptane-toluene. As pressure and hydrogen recycle are increased, the equilibriums become less favorable, particularly for the conversion of *n*-heptane, which requires a temperature about 75°F higher than methylcyclohexane does. As a result, potential gasoline yield at any given octane level is reduced. A compromise must be made between catalyst life (or frequency of regeneration) and yield of reformate at a given octane. For the several catalysts, typical operating conditions are given in Table 8-3. For nonregenerative operations, platinum catalysts are used at hydrogen-recycle rates and pressures in the higher

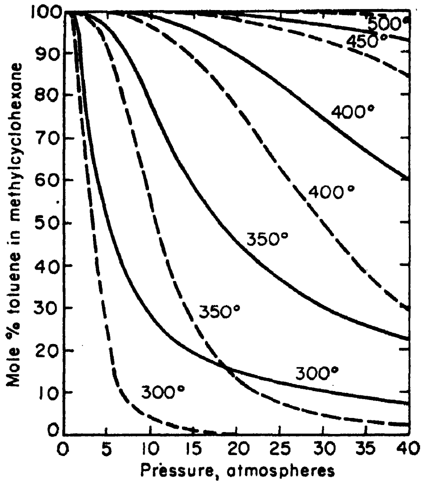

FIG. 8-3. Thermodynamic equilibria between methylcyclohexane and toluene (20). Broken lines: infinite hydrogen dilution; solid lines: no added hydrogen.

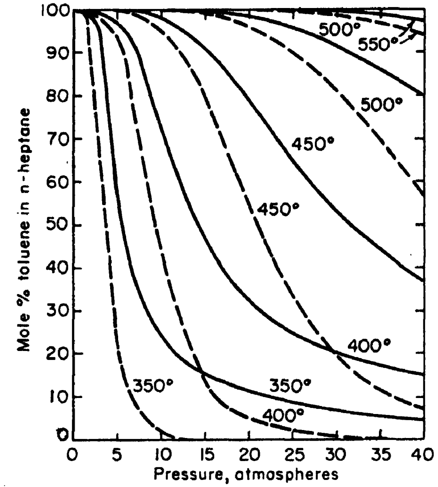

FIG. 8-4. Thermodynamic equilibria between *n*-heptane and toluene (20). Broken lines: infinite hydrogen dilution; solid lines: no added hydrogen.

Table 8-3

Catalyst	Pressure, psi	Recycle gas, scf/bbl	Average temperature, °F	Space velocity, wt/hr/wt
Platinum...............	200–700	4,000–13,000	850–950	1.5
Molybdena.............	200	2,500–8,000	900–950	0.5
Chromia...............	175	6,000	950–1050	0.7
Cobalt molybdate.......	400	3,600	800–900	1.0

ends of the indicated ranges. In all processes, lower pressures are permissible with lower-boiling feeds, which have lower tendencies to form coke than do higher-boiling stocks.

Rate Constants. Rate constants have been determined (27) for a platinum catalyst at low conversions where equilibrium considerations are not important. As shown in Table 8-4, the conversion of alkylcyclohexanes to aromatics is much faster than any other reaction. Although alkylcyclopentanes are converted to aromatics much more slowly (the rate is controlled by the rate of isomerization to alkylcyclohexanes), they are converted to aromatics two to three times as fast as is *n*-heptane. At low conversions, the principal effect of increasing the pressure from 200 psi to 500 psi is to reduce the rate at which paraffins are aromatized and increase the rate at which they are hydrocracked. Both of these effects reduce the yield of aromatics.

Table 8-4. Relative Reaction Rates over Platinum Catalysts (27)

Temp., °F	Press., psi	Reactions of naphthenes		Reactions of *n*-heptane		
		Dehydrogenation of methylcyclohexane	Isomerization of dimethylcyclopentanes	Dehydrocyclization	Hydrocracking	Isomerization
925	500	100	. . .	4	11	17
925	350	100	. . .	5	8	16
925	200	100	14	6	5	14
875	500	. . .	. . .	1	5	13
875	200	. . .	. . .	2	4	9

Equilibrium Limitations. At higher conversions, the effect of pressure is more pronounced. The relationship between conversion and pressure is shown in Fig. 8-5, in which the ratio of hydrocracking to aromatization in the reforming of heptanes* is plotted against the disappearance of heptanes. At 925°F and 200 psi, the ratio is constant over the range of 50 to 100 per cent conversion. At the same temperature, but at 350 psi, the ratio is higher, and it increases with conversion. Still higher ratios and greater increases are obtained at 500 psi. Thus, it appears that equilibrium considerations come into play at pressures above 200 psi. Reducing the temperature from 925 to 875°F increases the relative rate of hydrocracking at 500 psi but it has no effect at 200 psi.

Particle Size of Catalyst. With very active catalysts, the interior portions may be ineffective because reaction occurs before the reactants can penetrate to the core. In this situation, the activity of the catalyst

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* Normal heptane was charged, but it was rapidly isomerized to a mixture of heptanes.

increases as the particle size is reduced. With platinum catalysts, the effect may be substantial. For the conversion of methylcyclohexane to toluene, the reaction rate for $\frac{1}{16}$-in.-diameter pellets was shown to be almost three times as fast as for $\frac{1}{8}$-in.-diameter pellets, and for 20–28 mesh catalyst, it was nine times as fast (27). For the conversion of heptane, which is a slower reaction, the effect is less; the reaction rate over the $\frac{1}{16}$-in. pellets was about 60 per cent faster than over the $\frac{1}{8}$-in. pellets. Because the conversion of paraffins is the slower reaction, the relative rates of converting heptane are more indicative of the actual effect on the reforming operation. With catalysts less active than platinum, particle size is probably not important, except, perhaps, for the dehydrogenation of cyclohexane derivatives (67).

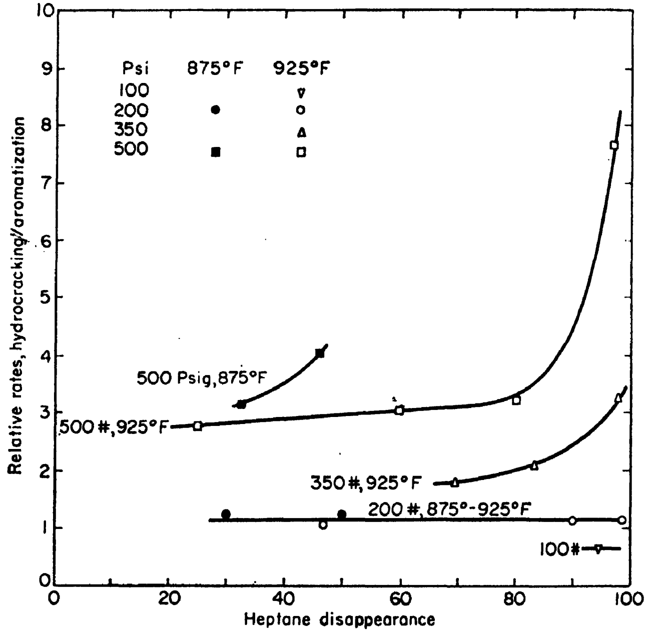

FIG. 8-5. Effect of pressure on relative rates of hydrocracking and aromatization of heptanes. NOTE: These data points were calculated from data taken from Hettinger et al. (27).

In choosing a particle size, catalyst activity must be balanced against pressure drop through the catalyst bed. For fixed beds, the diameter is usually between $\frac{1}{16}$ in. and $\frac{1}{8}$ in., and the length is usually equal to or somewhat greater than the diameter.

Trace Materials

Because catalytic reformers operate under substantial hydrogen pressures, "foreign" materials, such as sulfur, nitrogen, halides, and oxygen, are hydrogenated out of the product. Sulfur, for example, is converted to hydrogen sulfide. A typical reaction is

$$CH_3—S—CH_2CH_2CH_3 + 2H_2 \rightarrow CH_4 + CH_3CH_2CH_3 + H_2S$$

Although foreign elements are removed almost quantitatively during reforming, they sometimes affect the catalyst. Platinum catalysts, in particular, are affected by trace amounts of sulfur, nitrogen, halides, and certain metals.

Sulfur. Above some threshold value, sulfur inhibits dehydrogenation and promotes hydrocracking over platinum catalysts (26,27,33). Too high a sulfur concentration, therefore, reduces the yield of liquid product (34). High concentrations of sulfur also accelerate deactivation of the catalysts, especially at low hydrogen pressures (18,33,34,60). Loss in yield increases with the octane rating of the product, inasmuch as increased hydrocracking (relative to dehydrogenation) becomes more deleterious the further the reactions proceed.

If the recycle gas stream is not scrubbed to remove hydrogen sulfide, the total sulfur charged to the reactor is several times the amount in the feed. On the basis of yield considerations only, scrubbing of recycle gas was recommended at a feed sulfur level of 0.05 weight per cent in an operation producing an 85-octane-number product over a platinum-on-silica-alumina catalyst, and feed desulfurization was recommended at a feed sulfur level of 0.5 per cent (18). However, corrosion experience (3,36,68) dictates reducing the sulfur contents of feeds to much lower levels.

Nitrogen. Nitrogen in feed stocks to platinum-catalyst units may inhibit dehydrocyclization of paraffins, and also hydrocracking, although ammonia is a temporary poison (27,35). Small concentrations of amines are stated to have little effect on a platinum-on-silica-alumina catalyst (18).

Halides. Halides promote the activity of a platinum-on-alumina catalyst, and some concentration in the catalyst is necessary for good operation (49). However, if the halide concentration becomes too high, excessive hydrocracking results. The concentration in the catalyst may change during operation, depending upon such factors as the halide and water concentrations of the feed and the temperature and pressure of operation. For any combination of these conditions, there is an equilibrium halide concentration in the catalyst (49). The concentration in the catalyst increases as the halide content of the feed increases, and decreases as the water content increases. Small quantities of water are sometimes added to the feed to prevent the halide levels from building up to an uneconomic point (7,49). The highest tolerable level for chlorides in feeds is indicated to be about 5 ppm (51); at higher levels hydrogen treating of the feed is said to be necessary.

Halides are not necessary when a silica-alumina base is used for the catalyst (17).

Water. The effect of water on platinum catalysts apparently is variable. If the catalyst has a silica-alumina base, there is little or no effect (18). With alumina-base catalysts, anomalous results have been reported (7,27,49).

Metals. Metals such as lead and arsenic may poison the catalyst. Catalyst poisoning in at least three commercial units has been traced to tetraethyllead (18). However, tetraethyllead can be excluded from reformers by good housekeeping practices. Arsenic is said to be a severe poison, although some catalysts are claimed to have a considerable tolerance for it (19,27).

Feed Stocks

Potential feed stocks for catalytic reforming are the various stocks or "naphthas" from which gasolines are blended. Because virgin naphthas are the lowest-octane materials blended into gasoline, they are the preferred charge stocks. If reforming the virgin naphthas does not raise the total gasoline to the desired octane level, coker naphthas may also be charged. If still more octane improvement is required, naphthas from severe cracking operations may be processed, even naphthas from catalytic cracking.

Most catalytic reformers are operated to give the desired octane improvement with the least conversion of gasoline to butanes and lighter materials. From this standpoint, virgin stocks rich in naphthenes are the preferred feeds, and high aromatics contents are undesirable.* Aromatics are essentially unchanged in reforming. Further, at higher operating pressures, the presence of aromatics retards the production of additional aromatics (27).

Because of their olefin contents, cracked stocks are improved less by catalytic reforming than are virgin stocks. Olefins first become saturated under the conditions used in catalytic reforming, and the resulting paraffinic and naphthenic compounds have lower octane ratings than did the original olefins. Thus, there is an octane loss that must be recouped before a net gain can be realized.

Product Characteristics

Products from catalytic reforming operations are excellent stocks for blending into gasoline, usually without any further treatment. They

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* Although aromatics in the feed are not desirable from the standpoint of maximizing octane *improvement*, aromatics in the feed do increase the octane of the feed and of the product. Therefore, a feed with a high aromatics content will give a high yield at a given octane.

are stable, high in octane, and low in sulfur and gum (9,32), and they respond well to the addition of tetraethyllead, as shown in Fig. 8-6. Chemically, they consist principally of paraffins and aromatics. In boiling range, a catalytic reformate is broader than the feed stock from which it is made. Lower-boiling fragments are produced by hydrocracking, higher-boiling components by dehydrogenation. (An aromatic compound generally boils at a temperature about 50°F higher than the paraffinic or naphthenic compound from which it is made.) Some condensation of aromatic or olefinic materials also may occur, to produce a trace of very high-boiling materials (20,25). Because high pressures favor hydrocracking and low pressures favor dehydrocyclization, products from higher-pressure operations are lower-boiling. Typical product boiling ranges are shown in Table 8-5.

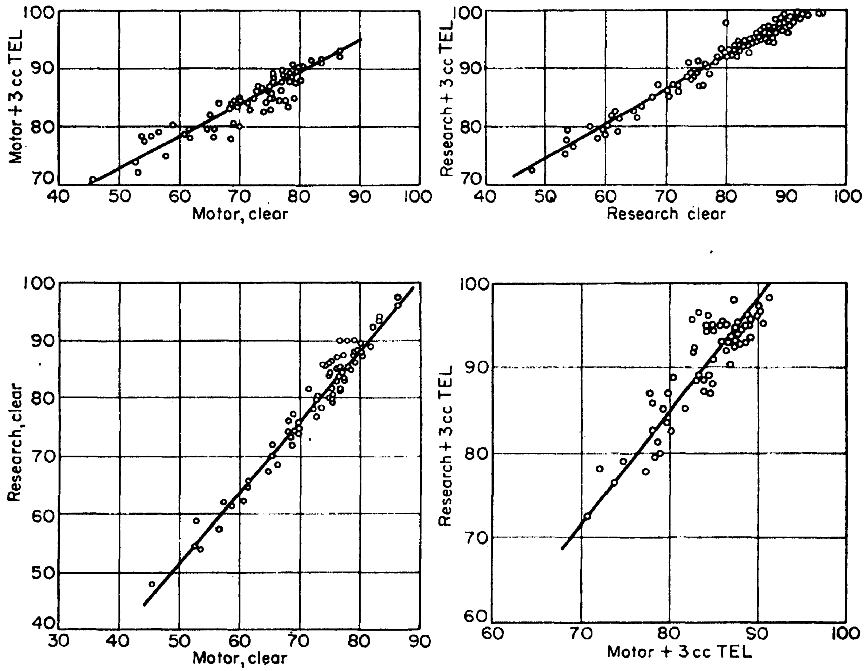

FIG. 8-6. Octane relationships of catalytic reformates (31).

Because hydrocracking lowers boiling points and dehydrogenation raises them, aromatics concentrate in the higher-boiling fractions of catalytic reformates. Consequently, the higher-boiling fractions have higher octane ratings (24).

Butanes produced in catalytic reforming are usually about 40 to 50 per cent *i*-butane; pentanes are about 55 to 65 per cent *i*-pentane (27,43).

Table 8-5. Typical Product Boiling Ranges

200-psig Operations (62)

	Feed	Products		Feed	Products		Feed	Product	Feed	Product
Octane, research, clear	36.5	85.0	95.0	51.0	85.0	95.0	43.4	95.0	29.6	85.0
Paraffins, %	49	....	....	34	....	....	59	....	65	
Naphthenes, %	43	....	....	43	....	....	28	....	19	
Aromatics, %	8	....	....	23	....	....	11	....	15	
10% off, °F	257	209	207	273	252	242	232	200	283	177
50% off, °F	291	285	288	306	303	298	260	258	310	270
90% off, °F	341	360	363	358	370	378	308	343	337	362
E.P., °F	373	448	457	385	437	455	336	390	355	419

275-psig Operations (11)

	Feed	Products		
Octane, research, clear	48.7	86.6	93.1	98.3
Paraffins, %	56	45	38	31
Naphthenes, %	41	1	0	0
Aromatics, %	12	52	60	68
10% off, °F	241	232	225	218
50% off, °F	260	265	267	268
90% off, °F	303	320	322	323
E.P., °F	332	365	374	373
RVP, lb	1.0	1.6	1.6	1.9

500-psig Operations (62)

	Feed	Products		Feed	Products		Feed	Products	
Octane, research, clear	36.5	85.0	95.0	51.0	85.0	95.0	43.4	85.0	95.0
Paraffins, %	49	....	....	34	....	....	59		
Naphthenes, %	43	....	....	43	....	....	28		
Aromatics, %	8	....	....	23	....	....	11		
10% off, °F	257	220	210	273	246	227	232	208	191
50% off, °F	291	286	281	306	298	291	260	261	256
90% off, °F	341	340	352	358	362	363	308	323	328
E.P., °F	373	414	420	385	432	440	336	378	387

Feed Preparation

As-produced feed stocks are sometimes not suitable for catalytic reformers, and feed-preparation operations may be required. The feed-preparation steps may consist of prefractionation, catalytic treatment to remove poisons, or both.

Prefractionation. Except where benzene is a primary product, materials lighter than heptanes do not make good feed stocks. No aromatics are produced from pentanes, and little, if any, benzene is produced from hexanes under the conditions used commercially. Consequently, it is generally desirable to exclude materials lighter than heptanes from the reformer charge, and a prefractionation step to remove light ends is often included in the reforming plant.

Because aromatics are higher-boiling than the corresponding naphthenes or paraffins, aromatics produced from high-boiling components sometimes boil outside the range of gasoline and must be fractionated from the product. Aromatics outside the gasoline range are usually less valuable than the materials from which they were produced. Also, they tend to form coke on the reforming catalyst and thus deactivate it. For these two reasons, fractionation to remove heavy ends from the feed is often desirable, the end point of the feed being controlled so that the product has the proper end point without further fractionation.

In some refineries, the feed to reforming is fractionated into cuts of different boiling ranges (37), and each cut is reformed under the conditions optimum for it.

Pretreating. Catalytic treatment of feed stocks is required only for platinum catalysts, which are sensitive to certain trace elements, such as sulfur, nitrogen, water, chloride, lead, and arsenic (18,19,27). Sulfur, nitrogen, chlorides, and metals can be removed from the feed by mild hydrogenation, usually over a cobalt-molybdenum catalyst;* the hydrogen required is available, of course, from the reforming operation. Sulfur and lead are eliminated from some virgin naphthas by a bauxite pretreatment at high temperatures (6,14,52), and arsenic is taken out by passing the feed through a bed of clay at atmospheric temperature (48,52). Arsenic and lead can also be removed by acid treating (22).

Types of Units

Because increasing hydrogen pressures retard the production both of coke and of aromatics, two kinds of units may be designed. Units may be designed to operate at pressures high enough to permit long runs without regeneration (or with infrequent, off-stream regeneration), or they may be designed to operate at lower pressures with frequent, on-stream regenerations. The higher-pressure type is cheaper to build, but it is less flexible than the lower-pressure type, is limited in product octane number, and gives lower yields at comparable octane levels. The choice between the two must be made by balancing a lower investment cost on the one hand against a higher yield and greater flexibility on the other. Of the processes announced so far, five (Platforming, Catforming, Houdriforming, Sovaforming, and a Sinclair-Baker process) employ high pressures to ensure long on-stream periods. Because

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* Hydrogen treating is discussed in Chap. 13.

platinum catalysts have the least tendency to induce catalyst deposits, all five of these processes use them. Of the six processes that regenerate the catalyst while on stream, only two (Ultraforming and Powerforming) use platinum catalysts. In Hydroforming and fluid Hydroforming, molybdena on alumina is used. Thermofor catalytic reforming employs chromia on alumina, and Hyperforming uses cobalt molybdate on alumina.*

Design Features. Catalytic reformers may be differentiated as to mechanical design. All five that do not employ on-stream regeneration are fixed-bed processes, as are three of the regenerative processes—the original Hydroforming process, Ultraforming, and Powerforming. Fluid Hydroforming employs fluidized beds, and the Thermofor and Hyperforming processes employ moving beds of catalyst.

The principal problem in the design of catalytic reformers is heat balance. Reactions which produce aromatics are very endothermic. Although these endothermic reactions are partially offset by hydrocracking reactions, which are exothermic, large amounts of heat must be supplied to the reaction zone. In fixed-bed units the heat is supplied by using several reactors in series, with intermediate reheating of the reactants. Because the most reactive compounds disappear first, the largest temperature drop occurs in the first reactor, with each subsequent reactor having a lower drop than its predecessor.

In fluid and moving-bed processes, heat is supplied by the recycle-gas stream, which is preheated to a high temperature. In fluid Hydroforming, all the recycle gas is charged to the base of the reactor and passes up through the fluidized bed; because of the rapid mixing of the catalyst, the temperature of the bed is substantially constant. In the moving-bed processes, there is no mixing of catalyst; therefore the hot recycle gas is admitted at several points in the bed. The catalyst is heated as it passes each point. Between points, the temperature of the catalyst drops by virtue of the endothermic reactions that occur.

Higher-pressure Platinum-catalyst Processes. A schematic flow sheet for a higher-pressure platinum unit is shown in Fig. 8-7. Typically, the feed is prefractionated to produce a sidestream of the desired boiling range, for example, 200 to 360°F in an ASTM distillation. Prefractionated feed is mixed with recycle gas, preheated, and charged to three or more reactors in series, with intermediate reheating. Effluent from the last reactor is cooled to condense the product, and a part of

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* Platforming was developed by Universal Oil Products Co., Catforming by Atlantic Refining Co., Houdriforming by Houdry Process Corp., Sovaforming and Thermofor Catalytic Reforming by Socony-Mobil Oil Co., Sinclair-Baker reforming by Sinclair Research Laboratories Inc. and Baker & Co., Ultraforming by Standard Oil Co. (Indiana), Powerforming, Hydroforming, and fluid Hydroforming by Standard Oil Co. (New Jersey), and Hyperforming by Union Oil Co.

the gas that separates is recycled. The net gas product is sent either to fuel or to facilities that recover condensibles. Reaction pressures in these reformers are usually between 500 and 750 psi (59), and a typical hydrogen-rich recycle-gas rate is 8,000 scf per bbl of feed. The catalyst may be regenerated occasionally by shutting the unit down and burning the carbonaceous deposit. To control the temperature, a mixture either of steam and air (30) or of flue gas and air (12) is used for combustion. Steam and air are employed for regenerating catalysts with a silica-alumina base; flue gas and air for catalysts with an alumina base.

Because higher-pressure platinum units are designed for long on-stream periods, great care is exercised to minimize the rate at which the catalyst deactivates. To avoid coking of traces of lubricating oils, for example, nonlubricated compressors are sometimes used to recycle hydrogen (45).

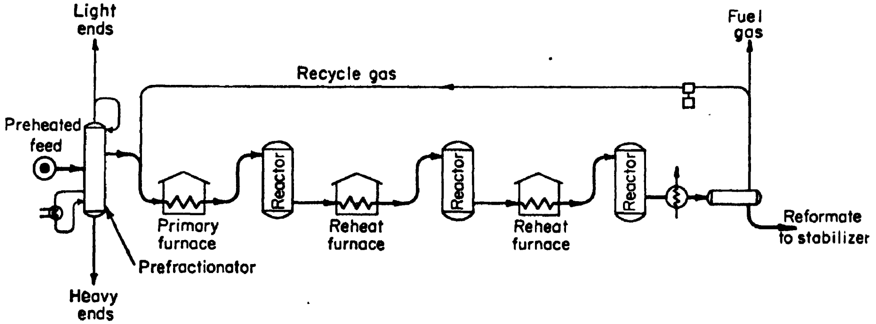

FIG. 8-7. High-pressure platinum-catalyst reforming unit.

Lower-pressure Platinum-catalyst Processes. Lower-pressure platinum reformers are similar to the higher-pressure type, except for the inclusion of facilities that permit on-stream regeneration. In addition to the regular on-stream reactors, such a unit includes a "swing" reactor so piped as to permit its substitution for any reactor which requires regeneration (54). Such units operate at pressures of 200 to 400 psi, with about 4,000 scf of hydrogen-rich recycle gas per barrel of feed. A special technique is required for regenerating the catalyst. The complete technique has not been disclosed, but it includes burning of the catalyst deposit (16,54).

Fluidized-bed Units.* Fluid Hydroformers have been built with the reactor and regenerator side by side and with the vessels stacked (15,56, 64,70). Fluid Hydroformers operate at pressures of 200 to 300 psi, with recycle gas rates of about 5,000 scf per bbl of feed. Reaction temperature is about 900°F. To maintain this temperature while supplying

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* The principles of fluidized beds are discussed in Chap. 5.

the endothermic heat of reaction, the recycle gas is heated to temperatures as high as 1200°F. (The feed temperature is held below 1000°F to minimize thermal cracking.) Cooling coils are provided in the regenerator to remove excess heat of combustion and thus hold the temperature at about 1100°F. Catalyst may be circulated at a rate of 1 lb per lb of naphtha charged. If higher circulation rates were used, more combustion heat could be transferred to the reactor, and the cooling coils in the regenerator could be eliminated. However, increasing the rate of circulation increases the demand for compressed air in the regenerator, because the molybdena in the circulating catalyst is reduced in the reactor and reoxidized in the regenerator. A method has been developed (63) to transfer all the heat of regeneration without increasing the air demand, but it has not been tried commercially. To achieve such transfer, a coarse inert material is circulated between the regenerator and the reactor at a rate independent of the rate of catalyst circulation.

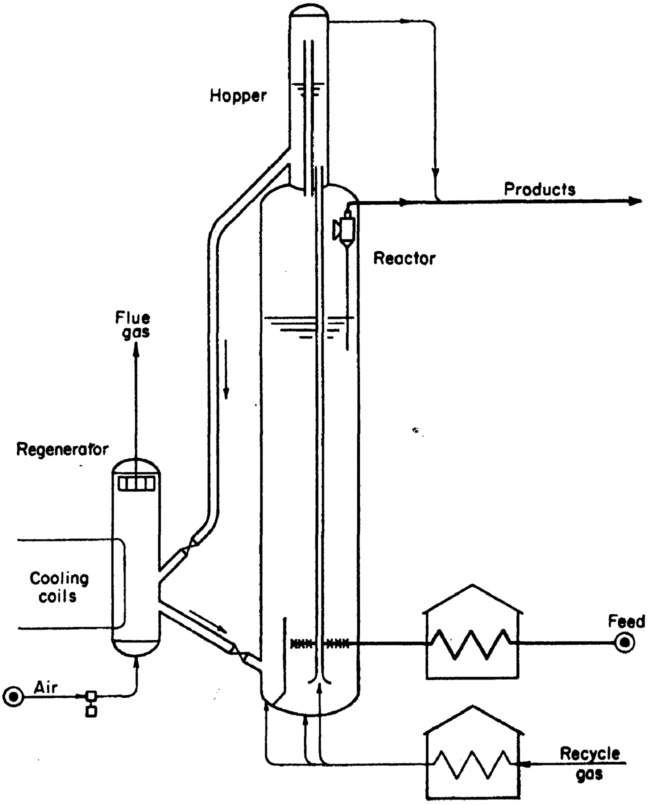

FIG. 8-8. Fluid Hydroformer.

A schematic flow sheet for a fluid Hydroformer is shown in Fig. 8-8.

Moving-bed Units.* Thermofor catalytic reformers and Hyperformers employ moving beds of catalyst. Only two commercial Thermofor units and one Hyperformer have been reported (47,61).

A Thermofor unit operates at about 175 psi. Reactor temperatures range between 950 and 1050°F, regenerator temperatures between 800 and 1050°F, and recycle gas rates between 2,500 and 8,000 scf per bbl of feed are used. As in fluid Hydroforming, the recycle gas is heated to 1150 to 1200°F to make up for the endothermic heat of reaction, and the feed is preheated to about 900°F. A typical catalyst circulation rate is 0.3 lb per lb of naphtha charged (39,47). The regeneration kiln operates at atmospheric pressure, and a lock-hopper system is used to remove catalyst from the base of the regenerator and to return it to the top of the reactor.

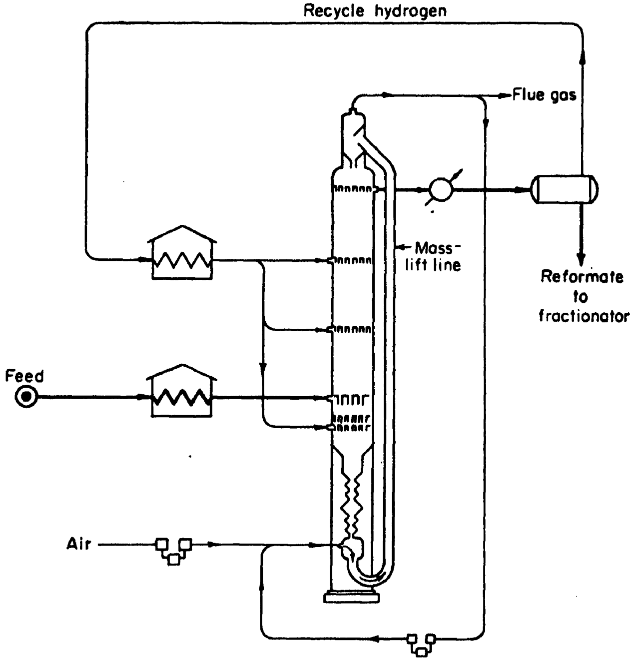

FIG. 8-9. Hyperforming unit.

The one commercial Hyperformer, illustrated in Fig. 8-9, operates at about 400 psi and 870°F, with a recycle gas rate of 3,600 scf per bbl of feed (5,61). Regeneration of the catalyst is accomplished in the Hyperflow lift system, where a mixture of inert gas and air, with about 2 per cent oxygen, functions both as a lifting medium and as a regeneration gas. Thus a separate regenerator is not required.

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* The principles of moving-bed units are described in Chap. 5.

Combination Processes

The octane potential of any of the reforming processes can be extended by the use of auxiliary extraction, adsorption, or thermal cracking facilities. The combination of extraction with Platforming is called "Rexforming" (21), while combinations of adsorption or thermal reforming with Houdriforming are called "Iso-Plus" (25,38). Process data are given in Table 8-6.

Table 8-6. Combination Catalytic Reforming Operations

	Rexforming results (21,29)							Iso-Plus results (38)			
	Feed[a]	Product	Feed	Products		Feed	Product	Feed	Products[b]		
									A	B	C
Composition, vol %:											
Paraffins	....	....	....	....	.....	....	.....	46			
Naphthenes	....	....	....	....	.....	12	.....	37			
Aromatics	9	56.1	8	56	77	3	59.2	17			
Boiling range, °F:											
10% off	264	183	270	180	189	268	167	230			
50% off	316	283	312	297	326	296	278	295			
90% off	374	372	370	382	392	351	345	365			
Gravity, °API	52.3	44.1	52.5	44.3	37.3	59.6	47.1	51.0			
Research octane, clear	33.0	97.5	30.0	95.2	101.8	10.3	101.0	54.1	100.0	100.0	100.0
C_5+ yield, vol %	....	80.1	....	82.9	76.8	....	68.2	....	81.9	79.1	77.8

[a] 1.5 per cent bottoms was removed from this feed before reforming.

[b] Includes polymer produced from olefinic gases. Cases A and B involve adsorption. In A, the raffinate is processed in a second reformer; in B, it is recycled to the first reformer. In C, the catalytic reformate is reformed thermally.

Extraction or Adsorption. Extraction and adsorption can be used to separate the aromatic product from a catalytic reformate, and the raffinate can be recycled (21,38). Such an operation has its greatest utility for higher-pressure processes, because it tends to offset the equilibrium limitations inherent in higher-pressure reforming. That it does not completely obviate the equilibrium barrier may be seen from the fact that better results are obtained if the raffinate is sent to a second reformer, instead of being recycled (38).

Recycling also minimizes overtreatment of light gasoline, inasmuch as the pentane-hexane cut can be separated from the recycle stream, and thus excluded from further treatment. Since little or no aromatics can be made from this fraction, further treating would result only in additional hydrocracking.

Thermal Reforming. Inasmuch as the production of aromatics is apparently limited by equilibrium considerations in higher-pressure operations, thermal reforming of a catalytic reformate gives better yields at high-octane numbers than does higher-pressure reforming all the way. When the equilibrium barrier is reached in catalytic reforming, further octane improvements can come only from hydrocracking, in which aromatics may even be destroyed. Thermal reforming at this stage produces olefins, which have higher octane ratings than the paraffins that would be made in high-pressure catalytic reforming (25). Also, aromatics are stable under thermal cracking conditions. For both reasons, the thermal reforming route should give superior results. Gases produced in thermal reforming contain olefins, which can be charged to polymerization or to alkylation. If the olefins are polymerized, the yields of gasoline are indicated to be only slightly lower than for extraction of the reformate, with recycle of the raffinate (25,38). If the olefins were alkylated, the yields via thermal reforming should be higher than for raffinate recycle.

A favorable factor for the thermal-reforming route is the availability of thermal-reforming facilities in most refineries.

Process Comparisons

The choice of a catalytic reforming process depends upon a large number of factors. Major ones include comparative yields, the practical octane "ceiling" for each process, investment costs, catalyst inventory costs, and operating costs. Where there is a use for hydrogen, its yield may be an important factor, and flexibility of operations is also of some importance. The choice has apparently narrowed to the several platinum-catalyst processes. No units designed for other catalysts have been built since 1955.

Liquid Yields. Yields from catalytic reforming depend on the characteristics of the feed, the octane level of the product, the type of catalyst, and the operating pressure. In most cases, the yield of debutanized product is of primary concern.* Generalized correlations of debutanized product yields are shown in Fig. 8-10 for operations with fresh platinum and with molybdena catalysts.† The platinum catalysts are the most selective, that is, they give the highest yields at a given operating pressure and product octane. Lower pressures give better yields.

For units designed to operate at higher pressures, the average gasoline yield is somewhat lower than the yield obtained with fresh catalyst.

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* Most modern refineries produce more butanes-butenes than can be blended into gasoline. In cases where there is a deficiency of butanes-butenes, the yield of depropanized reformate is of prime importance.

† A later publication (71) of yields over a platinum catalyst at 600 psi shows higher yields at lower Watson factors and lower yields at higher Watson factors than are indicated by Fig. 8-10.

The activity of the catalyst declines with time on stream, and at some activity level—40 per cent of fresh catalyst activity, for example (58)—the selectivity of the catalyst declines, so that gasoline yield at a given octane level is reduced. To determine the optimum length of the reaction period, an economic balance must be made of catalyst costs against gasoline losses (58,70).

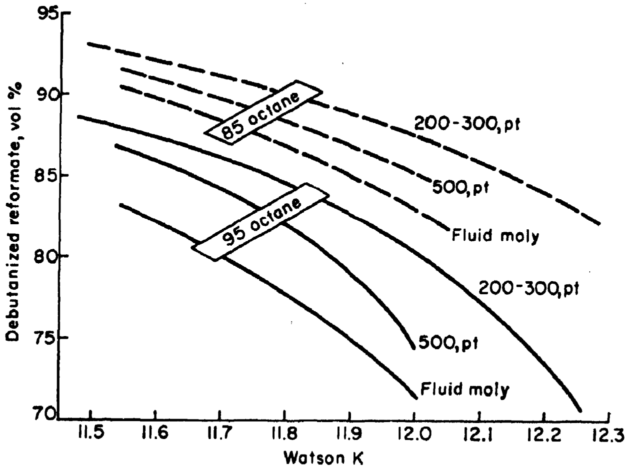

FIG. 8-10. Comparison of yields in catalytic reforming (55).

Basically, yield differences result from differences in the relative rates of hydrocracking and aromatization, and these rates are determined by the catalyst and the particular operating conditions used. As might be expected, the yield differences increase as the feed becomes more paraffinic and as the octane of the product increases. Both of these conditions make it necessary to reform more intensely.

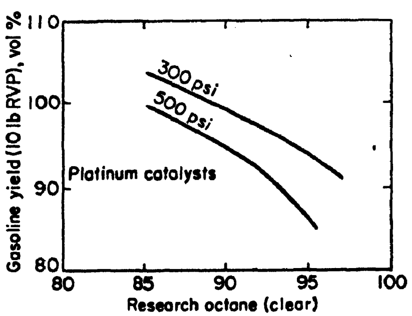

FIG. 8-11. Comparison of reforming yields (55).

Octane Limitations. As reforming is carried out to higher and higher octane levels, each additional increment is harder to obtain, and yields drop off at an increasing rate. For each combination of feed stock and process, there is an octane level above which yield losses would be prohibitive. This level may be considered the octane ceiling of the process. Typical yield-octane curves for two platinum processes are shown in Fig. 8-11 for a Mid-Continent naphtha. It is evident that the octane ceiling of the low-pressure platinum process is higher. At least one low-pressure platinum-catalyst unit is operated to make a product of 100 research octane number (clear) on a regular basis (68).

Investment Costs. In any given situation, the relative investment costs for the several processes depend upon the intensity of the operation, the characteristics of the feed stock, and the size of the unit. All these factors must be considered for each particular situation.

Comparative investment costs have been published for high-pressure and low-pressure platinum-catalyst units, and for fluid Hydroforming units (59). When operating at low intensities,* high-pressure platinum units are the lowest cost, followed by low-pressure platinum, and then by fluid Hydroforming. As the octane level rises, the costs for low-pressure platinum units and fluid Hydroforming units retain their same relative positions, but the cost of high-pressure platinum units increases more rapidly because recycle gas requirements increase sharply as octanes are raised. With a typical feed stock (say 50 per cent paraffins) and a product octane of 85 research octane (clear), a high-pressure unit may cost 20 per cent less than a low-pressure unit. On the other hand, a high-pressure unit may be more expensive when reforming the same feed to a research octane level of 95, clear. Thus the relative investment costs depend upon the intensity of the design operation. At any given octane level, feed-stock characteristics determine the reforming intensities required. Paraffin content is the principal factor in this regard.

Such feed-stock properties as sulfur, nitrogen, chloride, and arsenic contents are also important in that they may require feed pretreatment for platinum operations, whereas feed pretreatment may not be required for other catalysts.

Catalyst Inventory Costs. Catalyst inventory costs are determined by the amount required and the unit cost. Although platinum catalysts are much more active than others, their higher unit costs more than offset the activity differences, and a greater investment is required (59). The importance of this difference depends in large measure on how the platinum inventory is considered. The platinum, which accounts for a major portion of the inventory cost, is a nondepreciating item, although its value may fluctuate. Thus the salvage values of platinum catalysts are high, whereas the salvage values of others are negligible.

Operating Costs. Inasmuch as all the platinum reforming processes operate at about the same conditions, their direct operating costs should be roughly the same. Combination units such as Rexforming and Iso-Plus are, of course, more expensive to operate. Published costs for a high-pressure platinum unit and for a Rexforming unit are shown

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* For example, when reforming a feed stock containing 50 per cent paraffins to a research octane level of 85, clear. With a less paraffinic stock, higher octanes may be reached, and for a more paraffinic stock, the limit is lower.

in Table 8-7. Exclusive of catalyst costs, operating costs for a lower-pressure regenerative unit are somewhat higher than for a high-pressure unit because labor costs are higher. However, catalyst costs should be appreciably lower (40).

Table 8-7. Direct Operating Costs for Catalytic Reforming, Cents per Barrel

	High-pressure platinum (42)		Rexforming (41)	
Research octane no., clear	95	95	100.8	98.0
Feed stock	Mid-Continent	Kuwait	Mid-Continent	Middle East
Charge rate, bbl per day	10,000	10,000	4,300	4,300
Labor ($2.75 per hr)	1.7	2.0	5.0	5.0
Laboratory	....	....	1.2	1.2
Utilities:				
Fuel (15 cents per MM Btu)	5.7	5.7	10.0	10.0
Power (0.8 cent per kwhr)	2.3	2.6	1.9	1.9
Steam (30 cents per 1,000 lb)	....	....	1.9	1.9
Water (1 cent per 1,000 gal)	0.7	0.9	1.5	1.5
Catalyst	6.7	10.8	5.8	5.8
Solvent	....	....	1.6	1.6
Maintenance (3% of investment)	2.4	2.7	5.2	5.2
Insurance and property taxes	1.6	1.8	2.3	2.3
Total	21.1	26.5	36.4	36.4

Hydrogen Yields. Where there is use for it, hydrogen is a valuable by-product of catalytic reforming—for the manufacture of ammonia, for example (65). In some instances, hydrogen may even be the primary product (1). When operating at any given pressure, platinum catalysts yield the most hydrogen, but hydrogen yields go down as the operating pressure is raised. In reforming a Mid-Continent naphtha to 93 research octane number, clear, 1,100 scf per bbl were obtained over a platinum catalyst at 300 psi, 900 scf per bbl over the same catalyst at 500 psi, and 700 scf per bbl were obtained in fluid Hydroforming at about 250 psi with a molybdena catalyst (54).

Flexibility of Operations. Because of their regeneration facilities, all the regenerative units are more flexible than the nonregenerative type. They can all process a wider variety of feed stocks and can tolerate upsets in operation. For example, if the catalyst should become coked because of an interruption in the flow of recycle gas, it can be regenerated rather than replaced. In comparison with other regenerative units employing other catalysts, regenerative-platinum units cannot handle as wide a variety of feed stocks, unless they are equipped with feed pretreaters, which remove potential catalyst poisons.

Other Applications

Although the principal use of catalytic reforming is to upgrade motor gasoline stocks, it also finds some application in the manufacture of blending stocks for aviation gasoline and in the production of aromatic solvents. These two types of operations are similar. They both charge low-boiling fractions to produce stocks rich in benzene, toluene, and xylenes. If aviation gasoline is the end product, the desired cut may be separated from the reformate by distillation, or the whole reformate may be used. If aromatics are the end products, they may be separated from the reformate by extraction, adsorption, or extractive distillation (46). Because aromatics (other than benzene) boil higher than the corresponding naphthenes and paraffins, aromatics may also be fractionated from the product if the feed is fractionated sharply to an end

Table 8-8. Typical Catalytic Reforming Operations to Produce Aromatics

Type of unit:							
Reactors	Fixed-bed	Fixed-bed		Fixed-bed			Fluid
Regeneration	None	Infrequent		Frequent[a]			Frequent
Catalyst	Platinum	Platinum		Platinum			Molybdena
Product	Toluene	Benzene-toluene	Xylenes	Benzene	Toluene	Xylenes	Benzene-toluene-xylenes
Pressure, psi	...	325	450	[a]	[a]	[a]	250
Inlet temp., °F	...	935	935	....	.....	.....	934
Recycle gas ratio, M/M	...	5/1	7.5/1				
Feed stock dist., °F:							
Initial point	202	150	235	....	.....	.....	214
End point	224	220	265	....	.....	.....	291
Feed stock comp., vol %:							
Paraffins	(28)	49	52	25.7	33.8	36.2	
Naphthenes	(62)	44	40	70.7	62.5	59.0	
Aromatics	(10)	7	8	3.6	3.7	4.8	
Product comp., vol %:							
Paraffins	...	53	52				
Naphthenes	...	4	0				
Aromatics	63	43	48	....	.....	.....	59
Production of aromatics, vol %:							
Of charge	50	32.0	33.8	51.6	56.6	60.0	44.9
Of theor. from naphthenes	95	87	101	79	100+	100+	
Min. paraffin cycliz'n, %	...	....	....	....	25	19	
Reference	...	8	8	62	62	62	32

[a] The type of operation and operating pressure were not indicated. In view of other data from similar processes, these data are believed to be low pressure (perhaps 200 psi) and under conditions requiring frequent regeneration.

point just below the boiling point of the desired aromatic. Thus, if toluene is the desired product, the naturally occurring toluene is excluded from the feed, together with all materials of the same volatility. Excluding the natural toluene in such a case reduces the yield obtainable.

Production of Aromatics. Because of their low end points, feed stocks for the production of aromatics have less tendency to produce coke than do other feeds. Consequently, reforming units can be operated at lower pressures on such stocks, and thus higher yields can be obtained. A pressure of 250 psi is used in a frequent-regeneration plant producing toluene and xylenes (37). With a benzene-toluene feed, a pressure of 300 to 350 psi is used in one infrequent-regeneration unit (8); when producing xylenes in the same unit, a pressure of 400 to 500 psi is employed. These pressures are consistent with a report that 275 to 325 psi gave good long-cycle performance in a pilot-plant run on a benzene-toluene feed containing 0.02 per cent sulfur (33). Increasing concentrations of sulfur were shown to increase the rate at which the catalyst deactivated, and thus to raise the minimum pressure at which satisfactory operation could be achieved. At the same pressure, increased concentrations of sulfur also reduced the yields of aromatics, and a further reduction would be suffered if the pressure were raised to obtain satisfactory long-cycle operation. Some typical aromatics operations are shown in Table 8-8.

Production of Avgas Components. For the manufacture of aviation gasolines, catalytic reformates are valuable because of their high F-4 octane ratings.* To obtain components for blending into aviation gasoline, catalytic reformates are usually fractionated to produce stocks rich in toluene, xylene, or both. These have F-4 ratings as high as 220 with 4.6 cc TEL. (For comparison, the highest F-4 gasoline specification is 145 with 4.6 cc TEL.) The F-3 ratings* of such cuts range from about 95 to above 100 (23,32,53). For comparison, the F-3 rating for the best grade of aviation gasoline is 115.

Design Considerations

The principle operating problems in catalytic reforming have resulted from hydrogen sulfide corrosion. Problems have also been experienced with failures of internal reactor linings, which resulted in hot spots on reactor shells. These problems have been solved by revising the design

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* The F-3, or "lean mixture," octane number is a measure of the performance of a fuel in cruising. The F-4, or "rich mixture," number indicates performance in periods of high power demand from the engine, in take-offs, for example. Most aviation gasoline is either 100–130 or 115–145. The first of each pair of numbers is the F-3 rating; the second is the F-4.

procedures. Fouling of preheat equipment has also caused difficulties, and chlorides in feed stocks have caused some corrosion (49).

Hydrogen Sulfide Attack. Hydrogen sulfide has caused severe reactor-plugging difficulties from scale carried into the reactors by the feed gases (2). Although sulfide corrosion had been anticipated, the reactor-plugging difficulties had not. On the basis of previous experience, a hard, adherent scale was expected. However, under the high hydrogen pressures used in reforming, a loose, brittle scale is formed, which flakes off the metal surfaces, especially during start-up operations (36). Solutions to the problem include reducing the sulfur in the feed to 20 ppm or less, using stainless steel at high temperatures, and aluminizing of exposed surfaces (3). In units unprotected against sulfide attack, periodic chemical cleaning has been employed (28,44).

Another way to combat the scale problem is to employ radial-flow reactors, with flow from an annulus at the outside of the cylindrical bed to a collecting pipe through the center. Any scale carried into this type of reactor falls to the bottom of the annulus. Sometimes the annular design is used only for the first reactors, because the first reactors, which are preceded by large preheaters, are most subject to scaling problems.

Reactor Liners. Most catalytic-reformer reactors are internally lined to reduce metal temperatures. With some units employing monolithic liners, bypassing of vapors behind the insulation has resulted in high shell temperatures. To eliminate this possibility, metallic liners inside the insulating liners have been recommended (48).

Other Design Features. Most reactors are operated downflow. Typically, the catalyst is supported on a layer of large alundum balls (¼ to ¾ in. in diameter), which provide a low-pressure-drop path to the discharge nozzle while maintaining uniform flow of vapors through the catalyst bed. Each catalyst bed is topped by a layer of alundum balls (e.g., 3 to 5 in. of ¾-in. alundum balls) to protect the catalyst from disturbance by high-velocity inlet vapors (30,68). Baffles across the inlet nozzles may also be used (68).

Units not equipped for frequent regeneration are often designed for the same average temperature in each reactor, with the intent of obtaining uniform catalyst deactivation rates. Inasmuch as later reactors have lower temperature differentials, they are designed for lower inlet temperatures (50).

Fouling of Preheat Equipment. Fouling of preheat exchangers and furnaces has been troublesome on some units (2,37). Such fouling is usually attributed to exposure of the feed to oxygen. It can be avoided by charging only freshly distilled feeds or by gas blanketing the feed tanks. Stripping of the feed with product gas also helps.

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CHAPTER 9

POLYMERIZATION AND ALKYLATION

With the introduction of cracking, the production of light gases increased greatly—and a new opportunity was created. Cracked gases are rich in olefins, which are chemically reactive, and technologists were challenged to convert them into something more valuable than fuel gas. Research took two paths: thermal conversions and catalytic conversions. The thermal work bore the earliest fruit, and a semicommercial plant went into operation in 1931 to make gasoline by polymerization.* When a full-scale plant was built in 1934,† thermal polymerization appeared to have great promise. However, the picture changed suddenly when catalytic processes were perfected a short time later.‡ For a brief period, there were sharp disagreements as to the merits of the two polymerization routes; however, the arguments were soon resolved in favor of the catalytic processes.

Polymerization causes olefins to combine with each other. In the late 1930s, alkylation processes were developed that cause olefins to react with isoparaffins. Thus twice as much gasoline is made from a given quantity of olefins. The gasoline products are of exceptionally high octane quality, and 60 plants were built to make "alkylates" for aviation gasoline during World War II.

Alkylation units are much more costly to build and to operate than are polymerization units. Consequently, polymerization was favored initially for the production of motor gasoline, even though it produces

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* At the Toledo refinery of the Pure Oil Co. (17).

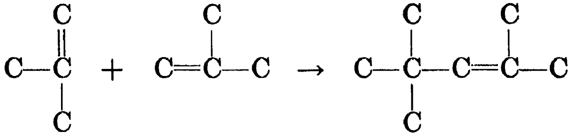
† At the Alamo refinery of the Phillips Petroleum Co. Cooperating companies included Standard Oil Co. (Indiana), Standard Oil Co. (New Jersey), The Texas Company, and M. W. Kellogg Co. (17).

‡ By Shell Oil Company (sulfuric acid catalyst) and by Universal Oil Products Co. (phosphoric acid on kieselguhr). Three additional processes were perfected later—one by Polymerization Process Corp. (copper pyrophosphate catalyst) and two by California Research Corp. (phosphoric acid on quartz and liquid phosphoric acid). Polymerization Process Corp. utilizes patents of Phillips Petroleum Co., Standard Oil Co. (Indiana), Standard Oil Co. (New Jersey), The Texas Company, and M. W. Kellogg Co.

less gasoline and the gasoline has a lower octane rating. Rising octane requirements brought alkylation into the motor-gasoline picture about 1955.

POLYMERIZATION

Although the term is sometimes used more broadly, "polymerization" usually means the combining of two or more olefinic molecules to yield a larger molecule. For example,

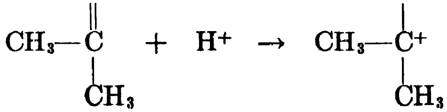


$$\mathrm{C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{\|}}{C}} + C{=}\overset{\overset{C}{|}}{C}{-}C \rightarrow C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}C{=}\overset{\overset{C}{|}}{C}{-}C}$$

When a mixture of olefins is polymerized, the operation is called "copolymerization." Under some conditions, reactants rearrange during reaction, and complex products are made. This type of polymerization is called "conjunct polymerization" (39). Conjunct products are not necessarily multiples of the original molecules, and they may contain paraffinic, naphthenic, and aromatic compounds as well as olefins. Operations in which the olefins do not rearrange are called "true" polymerization. Thermal polymerization is conjunct polymerization. Under the conditions used commercially, catalytic polymerization is true polymerization.

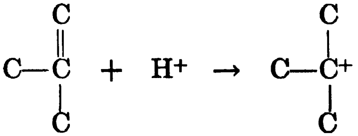
Reaction Mechanisms

As discussed in Chap. 6, thermal polymerization is believed to proceed by way of a free-radical mechanism. Catalytic polymerization, on the other hand, is explained by a carbonium-ion theory (39). A carbonium ion is formed by combination of an olefin with a proton furnished by the acid catalyst. With isobutene,



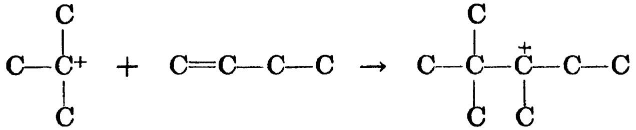
$$\mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}} + H^+ \rightarrow CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}}}$$

which is also written:



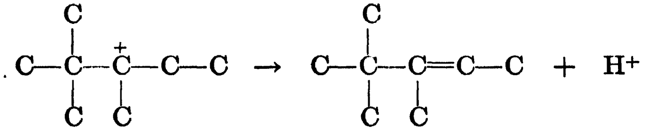
$$\mathrm{C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{\|}}{C}} + H^+ \rightarrow C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C^+}}}$$

The carbonium ion so formed may add to another olefin to form a larger carbonium ion. For example,



$$\mathrm{C{-}\overset{C}{\underset{C}{C^{+}}} + C{=}C{-}C{-}C \rightarrow C{-}\overset{C}{\underset{C}{C}}{-}\overset{+}{\underset{C}{C}}{-}C{-}C}$$

The larger carbonium ion may add another olefin to form a still larger ion, and a mixture of carbonium ions of various sizes results. Any of the carbonium ions may lose a proton to form an olefin. For example,



$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{+}{\underset{C}{C}}{-}C{-}C \rightarrow C{-}\overset{C}{\underset{C}{C}}{-}\underset{C}{C}{=}C{-}C + H^{+}}$$

Thus, the original proton is regenerated, and the cycle is repeated many times, a chain reaction resulting. Because carbonium ions may isomerize (especially when they contain tertiary carbon atoms), most products contain mixtures of isomers.

Thermal Polymerization

Like all pyrolytic processes, thermal polymerization is a complex process involving cracking, dehydrogenation, and cyclization reactions, as well as polymerization. Accordingly it can be performed with any light feed stock, whether olefinic or paraffinic. Although gasoline can be produced from any hydrocarbon, very severe conditions are required for paraffinic gases lighter than butane, and the lighter gases are seldom processed (21).

In any given situation, it is not necessary to convert all the butanes and butenes produced in a refinery, because they can be blended into gasoline up to a concentration of about 10 per cent. So long as the excess C_4 production does not exceed the production of butenes, the excess can be converted to gasoline by catalytic polymerization. In this situation, thermal polymerization cannot compete. Where excess C_4's exceed the butene production, alkylation can be used, since alkylation converts one mole of isobutane with every mole of butene. The field for thermal polymerization is limited, therefore, to situations where olefins are not available. Thermal-polymerization operations are discussed in Chap. 6.

Sulfuric Acid Polymerization

The first catalytic polymerization process employed sulfuric acid as the catalyst. Now known as the "cold acid" process, it polymerizes *i*-butene selectively (18). A later modification, the "hot acid" process, copolymerizes all the butenes. The cold-acid process was important during World War II (and still is) in preparing feed stocks for the manufacture of butadiene. *i*-Butene, which interferes with the production of butadiene, is removed from butanes-butenes via the cold-acid route.

Schematic flow sheets for the sulfuric acid processes are shown in Fig. 9-1. The cold-acid process consists of two steps: extraction of *i*-butene, followed by polymerization (49). As discussed in Chap. 4, extraction is accomplished with 65 per cent sulfuric acid at 70 to 100°F, usually in two stages. The extract phase is separated and heated to about 210°F for about 1 min to effect polymerization. It is then cooled to about 100°F and the product is separated from the acid catalyst by settling. Conversion of *i*-butene is generally about 90 per cent. The product is 75 per cent dimer; the rest is trimer.

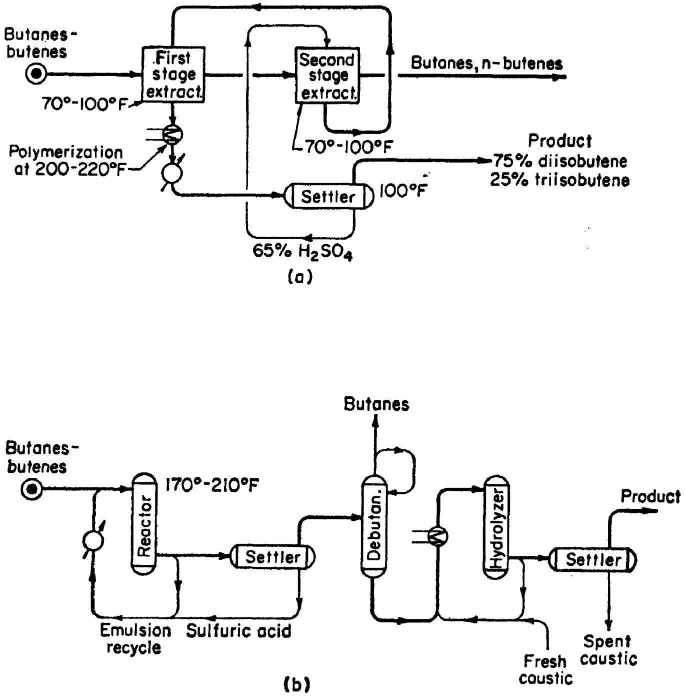


FIG. 9-1. Sulfuric acid polymerization processes. (*a*) Cold-acid process. (*b*) Hot-acid process.

In hot-acid plants, extraction and polymerization are carried out in a single step at about 200°F (49). A hydrocarbon-acid emulsion is circulated through the reactor to reduce the concentration of isobutene in the feed; circulation promotes copolymerization of the more-reactive *i*-butene with the less-reactive *n*-butenes and thereby improves yields.

Reactor effluent is settled to separate product from the catalyst, which is recycled. The product is fractionated to eliminate butanes and then hydrolyzed with caustic to break down any acidic materials. At contact times of 10 to 15 min, all the *i*-butene and an equal amount of *n*-butenes are converted. The product contains 90 to 95 per cent octenes.

During World War II, products from sulfuric acid plants were fractionated to separate the dimers, which were then hydrogenated to produce aviation-gasoline components (50). Except for those plants which prepared feed stock for butadiene production, cold-acid plants were converted to hot-acid plants during the war, because of the higher production from the latter.

Polymerization with Phosphorus-containing Catalysts

Four polymerization processes employ catalysts containing phosphorus. Three of them use solid catalysts; the fourth employs liquid phosphoric acid. As shown schematically in Fig. 9-2, an olefin-containing feed is first pretreated to remove sulfur compounds and poisons. It is then passed over a bed of catalyst at a temperature in the range of 300 to 425°F and a pressure in the range of 150 to 1,200 psi. Olefin conversions to gasoline are 85 per cent or better. There is a large exothermic heat of reaction—about 400 Btu per lb of butene reacted, about 670 Btu per lb of propene (13)—and olefin-lean streams are often recycled to act as heat absorbers and thus to help control the reaction temperature.

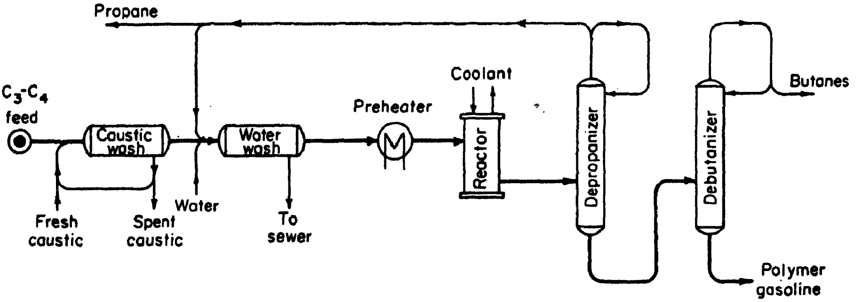


FIG. 9-2. Phosphoric acid polymerization unit.

Most units employ solid catalysts. The earliest operated at about 200 psi and at inlet temperatures of 450°F, rising to 500°F at the outlet. Under these conditions, coke is deposited on the catalyst, necessitating periodic shutdowns to burn it off.* Subsequently, it was found that coke production is greatly reduced at higher pressures, presumably

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* Combustion was carried out at temperatures controlled between 650 and 950°F. The catalyst was then steamed at 500°F for 6 to 16 hr to restore its normal water content (1,21,49).

because the denser reactants dissolve trace materials that would otherwise remain on the catalyst to be converted to coke (13,17). Most later units employ this principle, and catalyst-regeneration facilities are not provided.

The use of liquid phosphoric acid as catalyst necessitates the use of special materials of construction to withstand corrosion (34). Use of a liquid catalyst permits temperature control by circulating the catalyst through a cooler. Consequently, recycle of olefin-lean streams is not needed to control reaction temperatures.

Catalysts. Commercial catalysts include phosphoric acid on kieselguhr, copper pyrophosphate on charcoal, phosphoric acid on quartz chips (13), and liquid phosphoric acid (34). The acid-on-kieselguhr catalyst was developed first, and it is the most active (13). Copper pyrophosphate has the disadvantage of requiring an induction period of one to two days; it is usually diluted with charcoal to reabsorb any phosphoric acid leached from it. Phosphoric acid on quartz (28–35 mesh) is the least active of the catalysts because of its small surface area. However, the catalyst is rugged and it is "replaced" simply by washing with water and then recoating with 75 per cent phosphoric acid (39). Occasionally, accumulated tarry deposits must be burned off the quartz support (13). To avoid corrosion difficulties, alloys must be used for all equipment that contacts hot phosphoric acid.

Catalyst life ranges between 100 and 200 gal of polymer per pound for phosphoric acid on kieselguhr and between 100 and 150 gal per lb for copper pyrophosphate (39). In a semicommercial unit, catalyst life in a liquid phosphoric acid operation exceeded 45 gal of polymer per pound of acid (34).

Feed Pretreatment. Feeds are pretreated to remove hydrogen sulfide and mercaptans, which would otherwise enter the product and thus reduce its octane rating (13). Any basic materials must also be excluded because they are catalyst poisons. Typically, a feed is washed with caustic to remove hydrogen sulfide and mercaptans, and then is washed with water to remove any organic bases and any carry-over of caustic as well. Because oxygen promotes the deposition of tarry materials on the catalyst (13,21), both the feed stock and the wash water should be free of oxygen. Steam condensate is often used.

If a feed contains large amounts of hydrogen sulfide or mercaptans, the use of a regenerative absorbent may be more economic than caustic washing; regenerative absorbents for hydrogen sulfide include ethanolamines and tripotassium phosphate (29). Caustic solutions containing "solutizers" are regenerative absorbents for mercaptans (28); they are discussed in Chap. 14.

With phosphoric acid-on-kieselguhr catalyst, the water content of the feed must be closely controlled. If the feed is too wet, the catalyst softens and the reactor may plug. If the feed is too dry, coke deposits on the catalyst, reducing its activity and increasing the pressure drop (17). Because the distribution of water between the catalyst and the reactants is a function of temperature and pressure, which vary from unit to unit, different water concentrations are required in the feeds to different units (21). Sometimes the liquid feed is saturated with water at a controlled temperature. In other cases, saturation water is insufficient, and additional water is injected into the feed (2,13).

Reaction Conditions. Conversions of olefins to polymers depend upon temperature, pressure, reaction time, catalyst activity, and the composition of the feed.

Reaction rates increase with temperature, but the magnitude of the effect depends on the catalyst. With liquid phosphoric acid, an increase of 100°F is required to double the rate (4). With phosphoric acid on kieselguhr, the reaction rate appears to double for an increase of 20°F (21). Higher temperatures also increase the rate at which tarry deposits accumulate on solid catalysts, and thus they shorten catalyst life. Temperatures between 300 and 425°F are usually employed (30,39).

Increasing pressure increases conversion, primarily by increasing contact time (4). Pressures are usually in the range of 400 to 1,500 psi although pressures as low as 150 psi are sometimes used with phosphoric acid-on-quartz catalyst (13,17,30). Higher pressures permit the use of lower temperatures and thus reduce the formation of heavy polymers and coke (17).

Reaction times must be long enough to give satisfactory conversions, but not so long as to cause the production of polymer chains too long to be included in gasoline (42). Reaction times are usually expressed reciprocally as space velocity; the usual range is 0.12 to 0.46 gal of total feed per hour per pound of catalyst (13,17).

Reaction rates differ for the several olefins. *i*-Butene is the most reactive, followed by butene-1, butene-2, and propene, in that order (13). *i*-Butene accelerates the polymerization of *n*-butenes, and butenes accelerate the polymerization of propene.

Reactors. In the design of polymerization reactors, the principal problem is temperature control; provision must be made to remove the large exothermic heat of reaction. Some of this heat is absorbed by the reactants, which are permitted to rise 15 to 100°F, depending upon the reaction system. However, only a part of the heat can be removed in this way, and other means must be used to dissipate the rest. To achieve this end, two types of reactors are employed with solid catalysts: chamber and tubular. With liquid phosphoric acid, packed columns are used as reactors, and the catalyst is circulated through an external cooler to remove the heat of reaction.

Chamber reactors are vertical cylindrical vessels containing several beds of catalyst 2 to 8 ft deep (30), with provisions for injecting a quench liquid between them. Quench liquid usually consists of recycled light ends, which are largely unreactive paraffins. If the fresh feed contains more than 25 per cent olefins, it may be diluted to that concentration with recycled light ends (17); in such cases only part of the combined feed may be heated to reaction temperatures and charged to the first bed, the rest being charged cold as quench liquid between the beds (30).

Tubular reactors are single-pass heat exchangers, with the catalyst contained in the tubes, which are 2 to 6 in. in diameter (17). When water is used as the coolant, it is converted to steam, and temperature is controlled by controlling the steam pressure. Because tubular reactors provide closer control of temperatures than do chamber reactors, they can tolerate higher olefin contents in the feed stocks, the maximum concentration depending upon the particular design. For any given operation, the catalyst lasts longer in a tubular unit (39). On the other hand, tubular reactors are more expensive to build, and charging and discharging of catalyst is more difficult. The catalyst is often removed by sluicing the tubes with water (36).

Chamber reactors usually operate at about 500 psi; tubular reactors operate at 700 to 1,200 psi (17).

Feed Stocks. Presumably, any olefin can be polymerized. For the production of motor gasoline, however, only butene and lighter materials are of interest; heavier olefins (up to about C_{10} or C_{11}) can be incorporated directly into gasoline. With sulfuric acid as the catalyst, butenes are the only light stocks that can be polymerized satisfactorily, although a conjunct polymer can be made from propene (13). With phosphoric acid catalysts, propene also is a satisfactory feed stock, and a conjunct polymer can be made from ethylene. Butadiene is undesirable in a feed because it tends to make long-chain polymers and because it accelerates the deposition of coke on the catalyst. Nevertheless, units have been designed to handle up to 3 per cent butadiene (13).

In most circumstances, feed stocks to polymerization are limited to olefins made as by-products of cracking operations. However, butanes have been cracked to make olefinic feeds as primary products (15), and during World War II *i*-butene was made in England by dehydrogenation of *i*-butane (13).

Operations. Most polymerization units operate to produce motor gasoline from olefin-containing C_3, C_4, or mixed C_3-C_4 streams. Since World War II, most units are operated for maximum conversion of olefins. To distinguish such operations from a wartime practice, they are called "nonselective."

Wartime "selective" polymerization was aimed at producing highly branched isooctenes for subsequent hydrogenation to aviation gasoline.*

Table 9-1

Olefinic feed stock	Polymerization	Reactor	Psi	Temperature	
				In	Out
C_4	Selective	Tubular	600	350	365
C_3, C_4, or C_3-C_4	Nonselective	Tubular	1,000	400	415
C_3, C_4, or C_3-C_4	Nonselective	Chamber	500	350	450
C_3, C_4, or C_3-C_4	Nonselective	Chamber	500	400	475

Highly branched isooctenes are made by reaction of *i*-butene with itself or with *n*-butenes (39). Conversions were carried only to the point where most of the *i*-butene—the most reactive olefin—had reacted. Selective polymerization may still be practiced in refineries that have both a polymerization unit and an alkylation unit, especially if the available olefins exceed the capacity of the alkylation unit (45). Butene-2, which polymerizes least readily, is the preferred stock for alkylation (12).

Reaction conditions differ with the feed stock, the type of reactor, and the type of reaction. Typical conditions are given in Table 9-1 (17,30,49). In Fig. 9-3, space velocity requirements are related to olefin conversions when a mixed C_3-C_4 feed is charged to a chamber-type unit employing a phosphoric acid-on-kieselguhr catalyst. In Fig. 9-4, olefin conversions are related to all the operating variables for a tubular-type unit employing copper pyrophosphate catalyst (43).

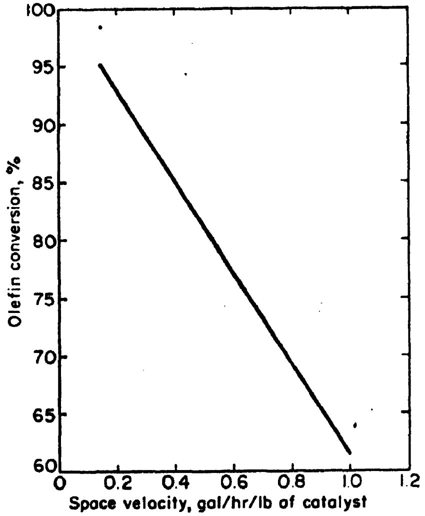

FIG. 9-3. Olefin conversions for chamber-type unit with phosphoric-acid-on-kieselguhr catalyst (31).

Products. Polymer gasolines are chemically stable, clean-burning fuels of high-octane quality. They are usually mixtures of polymers, principally dimers and trimers. With a propene feed, trimers pre-

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* The hydrogenated product has a clear motor octane rating of about 95 (17,30).

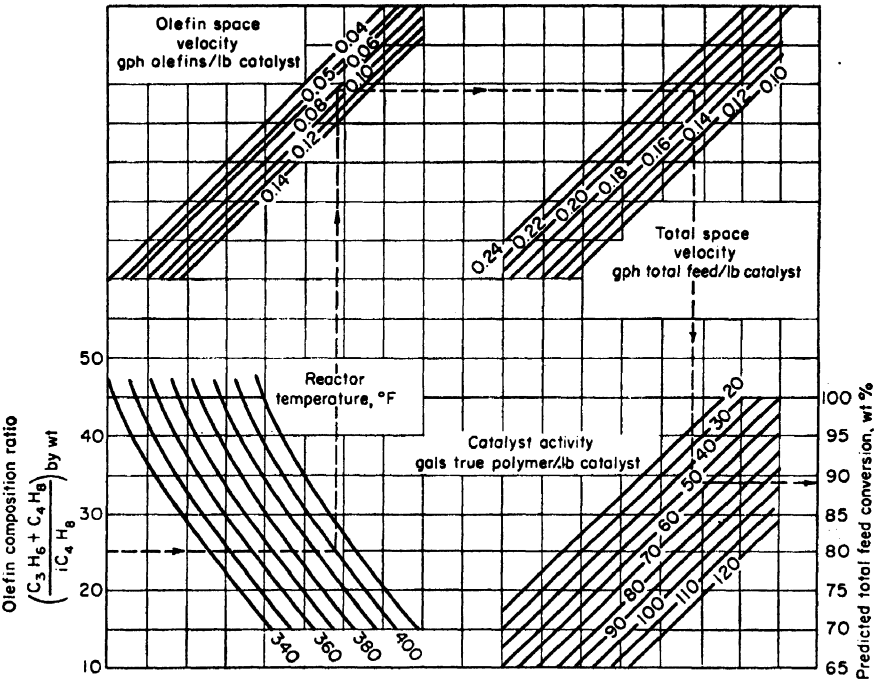

FIG. 9-4. Polymerization with copper pyrophosphate catalyst (43).

Table 9-2. Inspections of Polymer Gasolines (13,17,49)

	Propene polymer[a]	Butene polymer	Mixed polymer
Octane ratings:			
Research, clear	93	99	97
Research, 3 cc TEL	99	100+	101
Motor, clear	80	81	83
Motor, 3 cc TEL	85	84	86
ASTM distillation, °F:			
IBP	222	140	132
10%	267	211	206
50%	311	242	271
90%	381	361	372
EP	408	443	439
Reid vapor pressure, lb	0.5	2.0	

[a] Five per cent bottoms were fractionated from this polymer.

dominate. With a butene feed, dimers are the major constituents. Typical product inspections are listed in Table 9-2.

Utilities Requirements. Utilities requirements for polymerization are modest. For a typical chamber unit charging mixed C_3-C_4's, utilities may be about as in Table 9-3 (38).

Table 9-3

Utility	*Per bbl of polymer*
Steam	620 lb
Power	0.8 kwhr
Cooling water	4,300 gal
Fuel gas	15 lb

Related Operations

Olefinic polymers are important raw materials for the manufacture of chemicals (13). To provide feed stocks for the manufacture of oxo alcohols, heptenes are fractionated from propene-butene polymer and nonenes are separated from propene polymer. Also, propene tetramer is used in the manufacture of detergents. When tetramer is made, lighter polymer is recycled for further conversion.

Because the operation can be carried out in the same equipment, alkylation of aromatics is related to phosphoric acid polymerization (13). In this operation, a large excess of the aromatic—usually benzene—is used to promote alkylation and to minimize polymerization.

ALKYLATION

Alkylation is any reaction in which an alkyl group is added to a compound; in petroleum refining, it normally means reaction of an olefin with an *i*-paraffin to produce a larger *i*-paraffin.

i-Paraffins can be alkylated without catalysts, but high temperatures and high pressures are required (12,22,47). Commercially, acid catalysts are employed.* Sulfuric acid and hydrogen fluoride—the two most important catalysts—are used to alkylate *i*-butane with propene and butenes, and sometimes with pentenes. Aluminum chloride is used to alkylate *i*-butane with ethylene.

Like polymerization, alkylation is highly exothermic; the theoretical reaction liberates 630 to 700 Btu per lb of *i*-butane reacting (19).

Alkylation Reactions

The principal reaction in alkylation is the coupling of an *i*-paraffin, customarily *i*-butane, with an olefin, such as propene or a butene.

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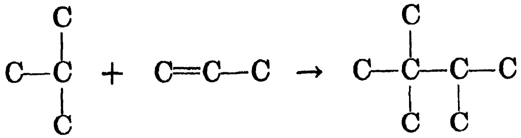
* One plant was built during World War II to alkylate ethylene with *i*-butane thermally to produce neohexane (20,22,47).

For example,

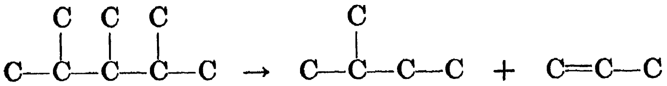


$$\mathrm{C{-}\overset{C}{\underset{C}{C}} + C{=}C{-}C \rightarrow C{-}\overset{C}{\underset{C}{C}}{-}\underset{C}{C}{-}C}$$

i-Butane Propene *i*-Heptane

In such an operation, the alkylation reaction competes with polymerization of the olefins. Inasmuch as trimers are formed in alkylation (19), some polymerization apparently takes place, followed by alkylation of the dimer.

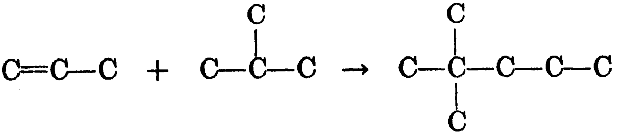
Polymerization reduces the consumption of *i*-butane. Other side reactions increase it, and some of them lead to the production of materials lighter than the theoretical products (12). For example, an alkylation product (or a reaction intermediate) may break down to form a smaller olefin and paraffin. With a butene feed the primary product may break down as follows:



$$\mathrm{C{-}\overset{C}{C}{-}\overset{C}{C}{-}\overset{C}{C}{-}C \rightarrow C{-}\overset{C}{C}{-}C{-}C + C{=}C{-}C}$$

Trimethylpentane *i*-Pentane Propene

The olefin so formed may then alkylate another molecule of *i*-butane:



$$\mathrm{C{=}C{-}C + C{-}\overset{C}{C}{-}C \rightarrow C{-}\overset{C}{\underset{C}{C}}{-}C{-}C{-}C}$$

Propene *i*-Butane *i*-Heptane

In the example cited, one mole of *i*-pentane and one of *i*-heptane result from the reaction of two moles of *i*-butane and one of butene.

Hydrogen transfer may also occur in alkylation, through a series of complicated reactions (12). With butene as the hydrogen acceptor, the over-all reaction may be represented as:

$$2C_4H_{10} + C_4H_8 \rightarrow C_8H_{18} + C_4H_{10}$$

i-Butane *n*-Butene *i*-Octane *n*-Butane

Although the major product is the same as from the theoretical reaction, twice as much *i*-butane is used to make it.

To some extent, hydrogen may transfer from one olefin to another, yielding a paraffin and a diolefin that associates with the acid catalyst. Further loss of hydrogen from diolefins results in highly unsaturated compounds that form "sludge" in the catalyst phase. Because sludge deactivates the catalyst, its concentration must be controlled. Accordingly, catalyst is withdrawn continuously and replaced with fresh or with regenerated material.

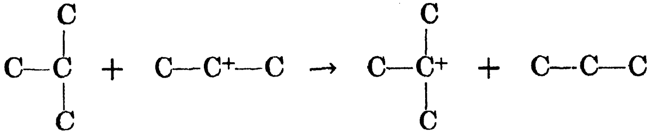
Although the chemical formula for the major product is the sum of the formulas of the reactants, the reaction is not simply the joining of the two molecules. The molecular structures of the products show clearly that isomerization must also occur.

Mechanism of Reaction

A number of theories have been advanced to explain catalytic alkylation (12). Probably the most popular is one involving carbonium ions. Carbonium ions result from unions of olefins with protons furnished by the acid catalyst:

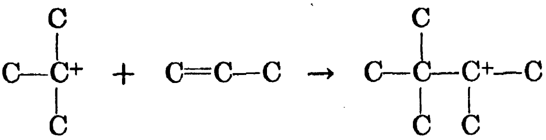
$$\mathrm{C{=}C{-}C} + \mathrm{H^{+}} \rightarrow \mathrm{C{-}C^{+}{-}C}$$

Carbonium ions react with *i*-butane to form *i*-butyl carbonium ions:



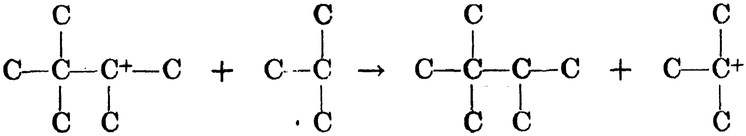
$$\mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C}}} + \mathrm{C-C^{+}-C} \rightarrow \mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C^{+}}}} + \mathrm{C-C-C}$$

i-Butyl carbonium ions combine with olefins to form larger carbonium ions:



$$\mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C^{+}}}} + \mathrm{C{=}C-C} \rightarrow \mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C}}-\underset{\underset{\textstyle C}{|}}{C^{+}}-C}$$

The larger carbonium ions react with isobutane to yield *i*-paraffins:



$$\mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C}}-\underset{\underset{\textstyle C}{|}}{C^{+}}-C} + \mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C}}} \rightarrow \mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C}}-\underset{\underset{\textstyle C}{|}}{C}-C} + \mathrm{C-\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle C}{|}}{C^{+}}}}$$

Thus, the *i*-butyl carbonium ion is regenerated, and a chain reaction commences.

The reaction intermediates—the larger carbonium ions—isomerize readily to other skeletal structures. This phenomenon explains the mixtures of isomers usually found in alkylation products.

Alkylation Catalysts

A large number of acidic materials have been used experimentally as catalysts for alkylation of *i*-paraffins (12). However, only sulfuric acid, hydrogen fluoride, and aluminum chloride have been used commercially.

Sulfuric Acid.* Sulfuric acid may be used with propene and higher-boiling olefins. (It reacts with ethylene to form ethyl hydrogen sulfate.) Commercially, the catalyst phase includes some water and some complex hydrocarbons, which are by-products of the reaction. A satisfactory catalyst contains at least 85 per cent titratable acidity, and a higher acidity is desirable (11,12). Below 85 per cent titratable acidity, acid usage increases sharply and product quality is lowered. Acidity is maintained at the desired level by withdrawing a part of the circulating stream and replacing it with fresh acid of about 98 per cent concentration. Replacement may be continuous, in which case the circulating acid is held at a desired acidity, usually 88 to 90 per cent. When batchwise replacement is used, acidity varies between that of the fresh and of the spent acids, usually between 98 and 88 per cent. Because the average acid strength is higher, somewhat better results are obtained with batchwise replacement, but more equipment is required.

Sulfuric acid catalyst is circulated as an emulsion with the reactants. Best results are obtained when the reactants are emulsified in the acid; such an emulsion results when the acid makes up at least 40 per cent of the mixture (19). Normally, the emulsion is held at about 50 per cent acid (12,45); higher proportions increase the difficulty of breaking the emulsion to recover the alkylation product.

The rate at which the catalyst deactivates depends mostly on the type of feed and the *i*-butane charge rate. Reported consumptions of acid have ranged from 0.3 to 2 lb per gal of product (19,30,32,45). Butene feeds have the lowest requirement; propene have the highest (30). For an operation with a butene feed and an *i*-butane:olefin ratio of 5:1, 0.9 lb of 98 per cent acid were consumed per gallon of product (19). For an operation on an effluent from a selective-polymerization unit and with an *i*-butane:olefin ratio of 12:1, an acid consumption of 0.3 lb per gal is claimed (32,45).

Hydrogen Fluoride.† Like sulfuric acid, hydrogen fluoride is used for the alkylation of *i*-butane with propene and higher-boiling olefins. High acidity is used to maintain high conversions and high antiknock quality (9). Unlike sulfuric acid, hydrogen fluoride is readily separated from water and sludge by distillation, and the optimum acidity is a function of fractionation costs. Typically, the circulating catalyst contains 85 to 92 per cent titratable acid and about 1.5 per cent water; the remainder is hydrocarbon sludge (12,26). If the catalyst contains

* Sulfuric acid alkylation was developed by the Anglo-Iranian Oil Co. (now British Petroleum), in cooperation with Humble Oil Co., Shell Development Co., Standard Oil Development Co., and The Texas Company (47).

† Hydrogen fluoride alkylation was pioneered by Phillips Petroleum Co. Universal Oil Products Co. have also developed an HF process (26).

as much as 5 per cent water, the quality of the alkylate deteriorates and the conversion decreases (9).

Hydrogen fluoride consumptions have been reported at from 0.2 to 0.8 lb per bbl of product (19,26).

Aluminum Chloride.* One plant was built during World War II to produce diisopropyl (for aviation gasoline) from *i*-butane and ethylene; it employs aluminum chloride–hydrocarbon complex as a catalyst (3,19). Hydrogen chloride is used as a promoter to increase and maintain catalyst activity (3). Because sludge gradually accumulates in the catalyst, some catalyst is withdrawn continuously and aluminum chloride is added to the remainder to hold the composition constant. The optimum aluminum chloride concentration in the catalyst is between 63 and 84 per cent (12).

Aluminum chloride requirements are about 1.4 to 3 lb per bbl of product (3), although laboratory experiments have required as little as 0.5 lb per bbl (12,46).

Process Variables

Important process variables in alkylation are the *i*-butane:olefin charge ratio, the *i*-butane content of the reactor effluent, temperature, and space velocity. Both product yields and product quality are affected by changes in these variables.

***i*-Butane-to-olefin Ratio.** Because the conditions which favor alkylation also favor polymerization of olefins, an excess of *i*-butane is employed to promote the desired reaction. Commercially, the ratios of *i*-butane to olefins charged to the reactors have ranged between about 4:1 and 12:1 (30,47), and ratios as high as 33:1 have been used experimentally (12). The usual commercial range is 5:1 to 10:1. Inasmuch as side reactions are reduced by increasing the *i*-butane charge rate, the octane rating of the product is improved, the end point is lowered, and the consumption of catalyst is reduced as the *i*-butane rate is increased.

Because alkylation reactions are rapid, internal circulation of the reactants may be used to augment the external *i*-butane-to-olefin ratio. Internal circulation consists of circulating the reactor contents rapidly and introducing the fresh feed into the circulating stream. Internal *i*-butane-to-olefin ratios may be as high as 1,000:1 (26).

***i*-Butane in Effluent.** Increasing the *i*-butane concentration in the reactor effluent has the same effect as increasing the *i*-butane:olefin ratio (19). *i*-Butane concentration may be increased by reducing the amount of *n*-butane charged to the reactors in the fresh feed and in the *i*-butane-recycle stream. Thus, there is an economic balance between

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* Aluminum-chloride alkylation is licensed by Phillips Petroleum Co. (26).

increasing the volume of the *i*-butane-recycle stream and increasing its purity.

Temperature. Low temperatures are used in all catalytic alkylations. Refrigeration is required with sulfuric acid, atmospheric temperatures are used with hydrogen fluoride, and slightly higher temperatures are employed with aluminum chloride.

With sulfuric acid, temperature is an important variable. From the standpoint of product quality, low temperatures are preferred; however, the catalyst is viscous at low temperatures and contacting it with the reactants is difficult (12). If temperatures are too low, yields are adversely affected (47); the lowest practical limit is about 30°F, and preferred temperatures are 40 to 50°F (19). The upper practical limit is about 70°F; at higher temperatures, the acid attacks olefins (12).

Hydrogen fluoride catalysis is less sensitive to temperature. In the laboratory, essentially the same results are obtained at −10°F and at 135°F (12). Reaction temperatures in the neighborhood of 75 to 100°F are convenient; consequently such temperatures are usually used (19). However, refrigeration has been used in at least two units, and improved octane ratings are claimed (9,25).

With the aluminum chloride catalyst, commercial operating temperatures are 110 to 140°F (12,46).

Olefin Space-velocity. Olefin space-velocity may be defined as the volume of olefin charged per hour divided by the volume of acid in the reactor. Reducing the olefin space-velocity improves the octane quality of the product, reduces the production of heavy materials, and lowers the consumption of acid (19).

Contact Time. Contact time is defined as the residence time of the fresh feed and externally recycled *i*-butane in the reactor. For sulfuric acid alkylation, the normal range is 5 to 40 min; for HF alkylation, it is 5 to 25 min. Long contact times in the absence of *i*-butane are undesirable, presumably because olefins, which are soluble in the catalyst, undergo side reactions. To minimize such reactions in the product settler (where catalyst is settled from the hydrocarbon product), an *i*-butane-rich stream may be bubbled through the acid phase, which, being heavier, is the lower phase (37).

Feed Stocks for Alkylation

Any olefin-containing hydrocarbon stream may be used to alkylate *i*-butane. Butenes are the usual alkylating agents, propenes are also used, and ethylene and pentenes are employed to a limited extent. Butene-*i*-butene copolymers have also been charged to alkylation, especially during World War II. Inasmuch as they react about as do butenes themselves (9), they must depolymerize before reacting.

The chief sources of olefins are cracking operations, especially catalytic cracking. However, olefins can be produced by the dehydrogenation of paraffins (8,27,33), and butanes are dehydrogenated commercially to provide feeds to alkylation (5,35). Butane is also isomerized to *i*-butane, which is cracked thermally to produce an alkylation feed (33). The production of ethylene is discussed in Chap. 6. In the commercial operation with aluminum chloride, an ethane-propane mixture is cracked, and the ethylene and propene are recovered by absorption in cold *i*-butane (3).

i-Butane is obtained from crude oils, from cracking operations, from catalytic reformers, and from natural gas fields. To supplement these sources, *n*-butane is sometimes isomerized. Isomerization is discussed in Chap. 10.

Alkylation feeds should be free of hydrogen sulfide and mercaptans (19). Both materials form free sulfur, which makes the product corrosive. They also lower leaded octane ratings of products and increase consumptions of catalyst.

Only small concentrations of diolefins are permissible in feeds to alkylation, with sulfuric acid catalyst at least. Diolefins increase the consumption of the catalyst (47).

Alkylation Products

Alkylation products—"alkylates"—are branched paraffins with high octane ratings. Butene alkylates produced with a sulfuric acid catalyst

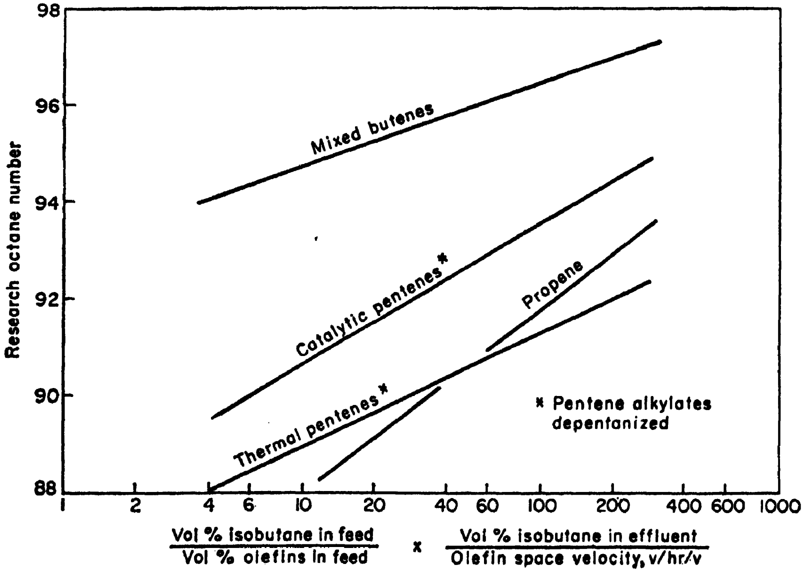


FIG. 9-5. Alkylate octane ratings (19.)

Table 9-4. Composition of a Typical Butene Alkylate (7,19)

Component	*Vol per cent*
Pentanes and lighter	8.9
2,3-Dimethylbutane	4.7
2-Methylpentane	1.1
3-Methylpentane	0.4
2,2-Dimethylpentane	0.2
2,4-Dimethylpentane	3.4
2,2,3-Trimethylbutane	0.2
2,3-Dimethylpentane	2.3
2-Methylhexane 3-Methylhexane	0.3
2,2,4-Trimethylpentane	24.3
2,2-Dimethylhexane	0.2
2,5-Dimethylhexane 2,4-Dimethylhexane	6.6
2,2,3-Trimethylpentane	1.2
2,3,4-Trimethylpentane	13.0
2,3,3-Trimethylpentane	12.3
2,3-Dimethylhexane	3.0
3,4-Dimethylhexane	0.4
2,2,5-Trimethylhexane	4.5
2,3,5-Trimethylhexane	0.9
High-boiling *i*-paraffins	12.1
	100.0

Table 9-5. Typical Inspections of Alkylates (19,27,30,45)

	H_2SO_4 Alkylates				HF Alkylates	
	Butene alkylate[a]	Propene alkylate[a]	Pentene alkylate[a]	Aviation alkylate[b]	Butene alkylate	Aviation alkylate
Gravity, °API	69	72	67	71	69	70
ASTM distillation °F:						
10%	197	179	227	164	199	200
50%	224	196	247	212	224	220
90%	261	241	281	230	264	239
End point	360	360	360	314	392	327
Octane ratings:						
Research, clear	95	89	90	...	93.1	91.6
Motor, clear	...	...	...	...	....	89.8
F-4 (4.6 cc TEL)	151	122	127	165		
RVP, lb	3.5	4.0	1.5	4.6	....	2.3

[a] Rerun to 360° end point; pentene alkylate is depentanized. Yields are 90 to 95 per cent of total alkylate.

[b] Produced from the effluent from a selective-polymerization plant (45).

usually rate 93 to 95 on a clear research basis, although ratings of 92 to 97 have been reported (30,31,45). With hydrogen fluoride catalyst, butene alkylates rate about 91 to 93 research octane clear (27,30). Addition of 3 cc TEL raises octane ratings by 10 to 12 units.

As shown in Fig. 9-5, variations in octane ratings in sulfuric acid alkylation can be related to variations in process conditions (19,51).

Table 9-6

Olefin	Alkylate, vol %	*i*-Butane, vol %
Ethylene	188	139
Propene	181	128
Butenes (mixed)	172	112
Pentenes (mixed)	165	96

Also, octane ratings of propene and pentene alkylates are somewhat lower than for butene alkylates.

When butene is the alkylating agent, the major components of the product are trimethylpentanes (12). With propene, the major components are dimethylpentanes, and with ethylene the principal product is diisopropyl (2,3-dimethylbutane). In all cases both lighter and heavier materials are also made. A typical composition of a butene alkylate is shown in Table 9-4. Some typical product inspections are given in Table 9-5.

Because an alkylate is denser than the reactants that form it, volumetric yields are not additive. The theoretical yields of alkylates and the theoretical isobutane requirements are given in Table 9-6 (based on olefin reacting). Theoretical yields are approximated commercially, even though reactions occur that consume more and less than the theoretical *i*-butane. Apparently, such reactions usually offset each other.

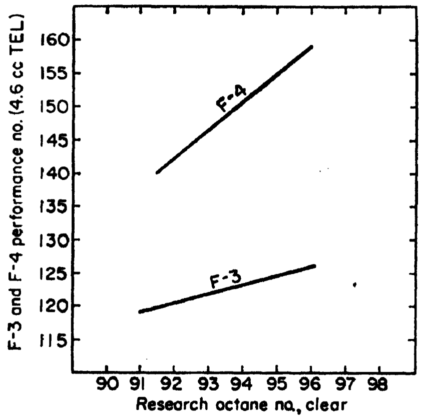
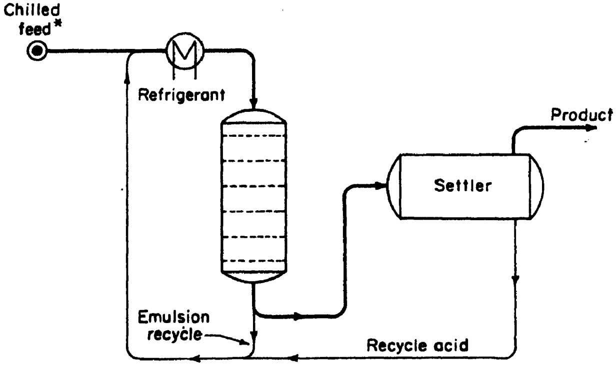


FIG. 9-6. Octane relationships for butene alkylates (19).

When alkylate is to be used as a blending stock for aviation gasoline, 5 to 10 per cent of heavy ends must first be separated to meet boiling-range specifications. Removing the heavy ends raises the octane rating inasmuch as the heavy ends have research octane ratings of about 80 to 85 (47). For aviation gasolines, the F-3 and F-4 octane scales are used. How aviation ratings of alkylates relate to research ratings is shown in Fig. 9-6.

Reaction Systems for Alkylation

Because *i*-butane is almost insoluble in the acid catalysts and because the olefins are relatively soluble, alkylation reaction systems must be designed for thorough mixing of the hydrocarbon and catalyst phases if polymerization is to be minimized (9). Also, provisions must be made for removing the high exothermic heat of reaction and the heat of mixing. Reactors in use include time-tank, jet, cascade, impeller, and tubular types. Heat is removed through cooling coils, which may be external or internal to the reactor, or by permitting part of the reactants to vaporize. The latter operation is called "autorefrigeration." Autorefrigeration is not used in hydrogen fluoride units because hydrogen fluoride is itself very volatile.



* Includes recycle isobutane

FIG. 9-7. Time-tank reactor system.

Time-tank and Jet Reactors. Time-tank and jet reactors were used in early sulfuric acid units. The time-tank system is illustrated in Fig. 9-7. Chilled feed is mixed with a recycle catalyst phase and pumped through a cooler and a cylindrical reactor fitted with internal perforated plates. As it leaves the reactor, the hydrocarbon is emulsified in the acid. Sufficient emulsion is circulated through a cooler to control the reaction temperature as desired. The remainder of the emulsion passes to a settler, where hydrocarbon product separates from the acid, which is recycled.

The jet reactor, illustrated in Fig. 9-8, operates on the same principle, except that jet devices provide the energy of mixing, and internal baffles are not used.

Cascade Reactor. The cascade system is also used in sulfuric acid plants. As shown in Fig. 9-9, a cascade reactor is divided into several compartments, each of which is mixed individually (44). *i*-Butane passes through all of the compartments in series, but the olefin-containing feed is divided among the several compartments; thus, the effective *i*-butane-to-olefin ratio is increased substantially. With this type of reactor, autorefrigeration is used for cooling. The hydrocarbon vapors that evolve function as a refrigerant; they are compressed, condensed, and flashed, and the liquid portion is returned to the reactor.

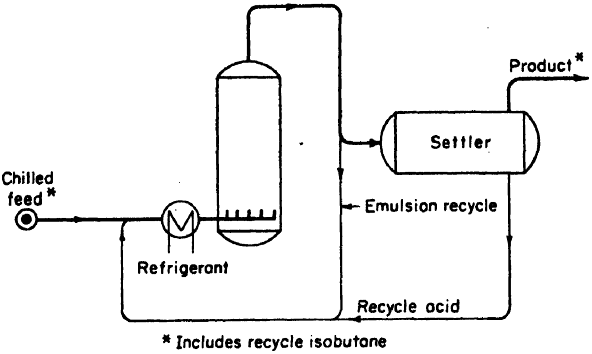


FIG. 9-8. Jet-type reactor system.

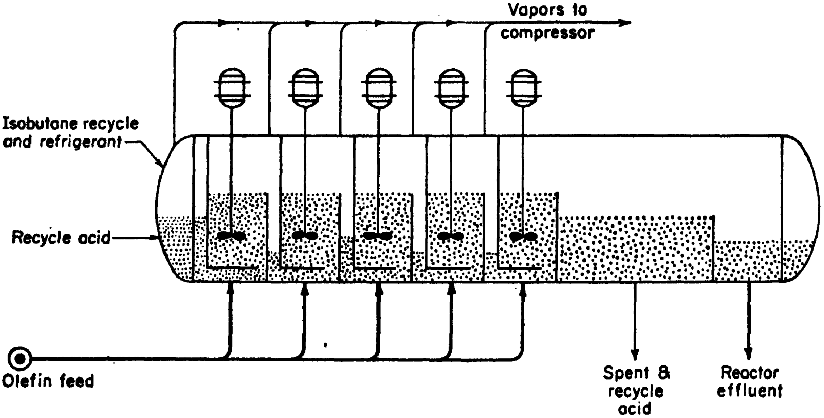


FIG. 9-9. Cascade reactor.

Power requirements for mixing are reported to be 0.002 to 0.004 hp-hr per bbl of product (14).

Impeller-type Reactor. The impeller-type reactor, illustrated in Fig. 9-10, is used in both sulfuric acid and hydrogen fluoride plants. Basically, it is a U-tube heat exchanger fitted with an impeller at one end to circulate an acid-hydrocarbon emulsion; an outer shell forms an annular return passage that permits the emulsion to circulate. In sulfuric acid units, refrigerant may be passed through the heat-exchange coils. Alternatively, *i*-butane may be used to advantage as the refrigerant; the system that employs this principle is called "effluent refrigeration" (45). As shown in Fig. 9-11, the refrigerant is mixed with the chilled feed stream, and reactor pressure is kept high enough to hold all the hydrocarbons in the liquid phase. Reactor effluent is settled and the hydrocarbon liquid that separates is flashed at a lower pressure; part of it vaporizes, and the temperature drops. The cold effluent then passes through the heat-exchange coils, and more of it vaporizes as it extracts heat from the reactants. Vapors, largely *i*-butane, are separated from the effluent and passed to a refrigeration system where they are liquified. The *i*-butane-rich condensate is then returned to the reactor. Inasmuch as the *i*-butane refrigerant passes through the whole reactor as liquid, it increases the effective *i*-butane-to-olefin ratio at little extra cost.

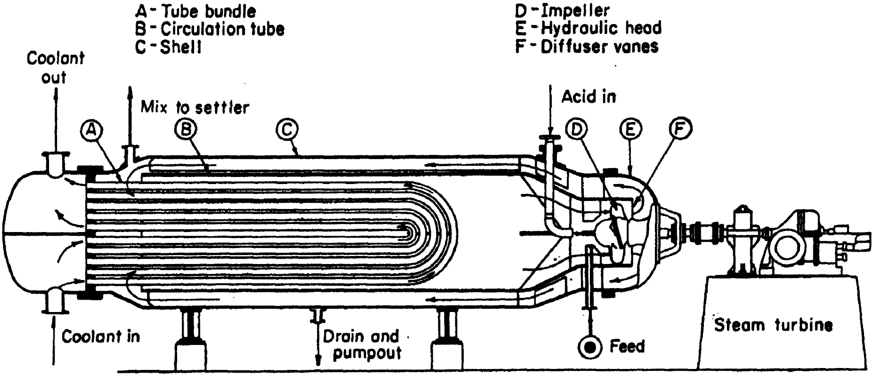
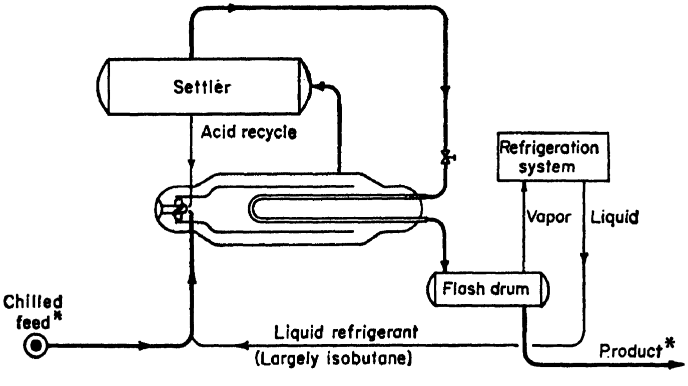


FIG. 9-10. Impeller reactor (Stratco contactor).



* Includes recycle isobutane

FIG. 9-11. Effluent-refrigeration system.

High internal circulation rates are used with impeller-type reactors; for example, internal flow rates may be 150 times the fresh-feed rate. As a result, over-all heat-transfer coefficients are usually quite high. When an impeller reactor is used, pumps are not needed to return recycle acid from the settler because the pressure rise across the impeller is large enough to overcome the pressure drop in the lines to and from the settler; however, care must be exercised in designing these lines.

Power requirements for mixing have been reported at 0.007 to 0.01 hp-hr per bbl of product for sulfuric acid units; at about 0.002 hp-hr per bbl for hydrogen fluoride units.

Tubular Reactors. In hydrogen fluoride units, simple tube-and-shell heat exchangers are sometimes used (24). Such reactors cannot be used in sulfuric acid units because sulfuric acid is too viscous for adequate mixing by this technique.

Alkylation Units

The basic elements of all alkylation units are the same. As shown in Figs. 9-12 and 9-13, facilities are needed to caustic-wash the feed to remove sulfur compounds, to contact the feed with recycle *i*-butane and with an acid catalyst while controlling the temperature, to settle the catalyst from the hydrocarbon product and recycle it, to remove traces of acid from the product, and to fractionate recycle *i*-butane from it. To prevent propane from building up in the recycle *i*-butane, a small depropanizer is usually provided to remove propane from a slip stream. Also, a debutanizer is usually included to separate *n*-butane from the product, and a rerun tower is required to remove heavy ends if the product is to be blended into aviation gasoline. Some older units require rerun towers for the production of satisfactory motor gasoline.

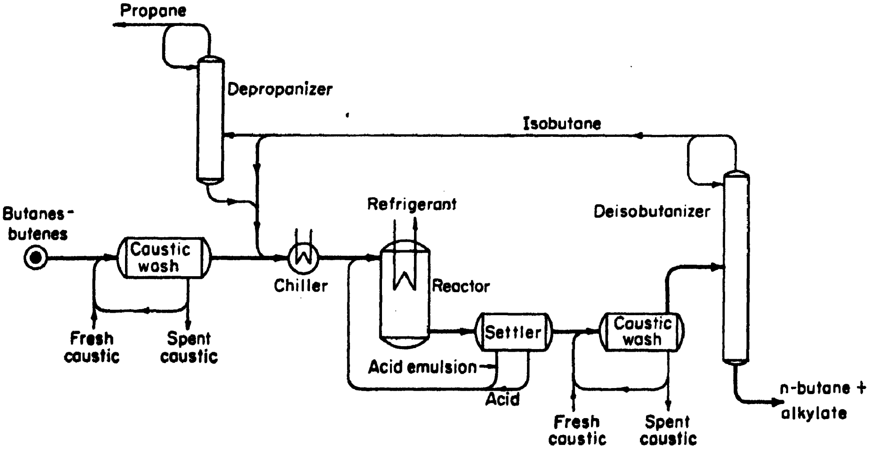


FIG. 9-12. Sulfuric acid alkylation.

As indicated in Fig. 9-12, a sulfuric acid unit also requires a refrigeration system to cool the reactants to the desired temperature, about 45°F, and to remove the heat of reaction and the heat of mixing at that temperature. Because hydrogen fluoride units operate satisfactorily at temperatures in the neighborhood of 100°F, they do not require refrigeration equipment. However, as shown in Fig. 9-13, they do require additional equipment to dry the feed stock, to strip hydrogen fluoride out of the product, to rerun a slip stream of the circulating catalyst to reject water* and tar, and to remove traces of fluorinated compounds from the product. Also, in the concentrations used commercially, hydrogen fluoride is somewhat corrosive, and some alloy protection is needed where aqueous hydrogen fluoride is encountered; monel is usually used (19).

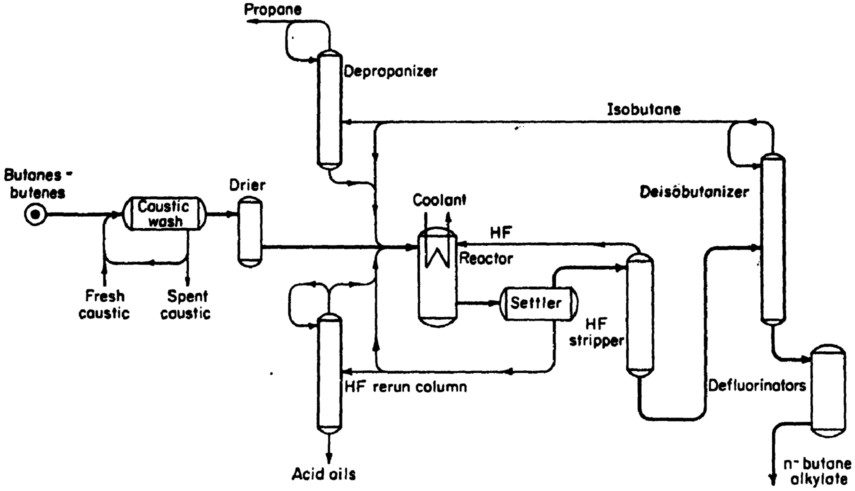


FIG. 9-13. Hydrogen fluoride alkylation.

Hydrogen fluoride is soluble in the hydrocarbon product to the extent of about 1 per cent. Various arrangements have been used to strip it out and to decompose traces of hydrofluorinated hydrocarbons (9,30). In the arrangement of Fig. 9-12, the reactor effluent is stripped in a column packed with aluminum rings, which function as packing and as a catalyst for decomposing the fluorides. Alternatively, the reactor effluent may be charged directly to the deisobutanizer. Then, the hydrogen fluoride is taken overhead in the deisobutanizer and in the depropanizer, and a stripper is used to recover hydrogen fluoride from the propane. In all cases, the product at some stage is passed through a bed of bauxite or a caustic wash to remove traces of fluoride.

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* Water and hydrogen fluoride form a maximum-boiling-point azeotrope containing 40 per cent hydrogen fluoride. The azeotrope is discarded.

The design of HF alkylation units is discussed in detail in "Hydrofluoric Acid Alkylation," published by the Phillips Petroleum Co. in 1946.

Utilities Requirements. Utilities requirements for alkylation are higher than for polymerization because of large requirements for fractionation and refrigeration. The utilities consumption in Table 9-7 have been reported per barrel of product (27,44). Fractionation facilities account for a large part of the utilities requirement, because sharp separations of large streams are required. For orientation purposes, Table 9-8 gives an approximate idea of the sharpness of separation necessary for the major towers.

Table 9-7

Steam, lb	700	8
Power, kwhr	3	2
Cooling water, gal	4,300	1,730
Fuel, 1,000,000 Btu	.....	1

Table 9-8

Fractionator	No. of trays	Reflux ratio
Depropanizer	22	8
Deisobutanizer	56	6
Debutanizer	22	1

Comparisons of Alkylation Units

Sulfuric acid and hydrogen fluoride units are competitive. They operate on the same feed stocks and produce similar products in the same yields.

With regard to octane potentials, sulfuric acid catalyst has an advantage in that somewhat higher-quality products can be made. However, operating costs increase as the octane of the product is increased.

The commercial use of hydrogen fluoride alkylation involves some industrial hazards; however, with proper precautions, excellent safety records have been achieved (10). In addition to adequate design and performance of all equipment, special precautions must be taken by all workmen in the immediate vicinity of the plant. Liberal use of protective clothing is required and diligence must be used to confine all hydrogen fluoride to the acid area; all equipment including protective clothing must be completely neutralized before it is taken from the area.

Freight costs may be a considerable factor when the refinery is located far from acid supplies. Inasmuch as hydrogen fluoride requirements are, at most, 10 per cent of sulfuric acid requirements on a weight basis, freight differences can be substantial. Also, spent sulfuric acid may represent a disposal problem; it may even have to be shipped back to the point of origin.

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CHAPTER 10

ISOMERIZATION

Surprisingly large differences in the properties of hydrocarbons result from small structural differences. *i*-Butane, for example, can be alkylated readily with olefins, but normal butane is unreactive. Also, as shown in Table 10-1, the octane numbers of paraffins and olefins are markedly affected by their degree of branching, and the octane number of an olefin depends also upon the position of the double bond. Thus, isomerization is of general interest in petroleum refining.

Table 10-1. Octane Ratings of Some Representative Light Hydrocarbons

Hydrocarbon	Research octane		Motor octane	
	Clear	3 cc TEL	Clear	3 cc TEL
n-Pentane	62	89	62	84
i-Pentane	92	109	90	105
n-Hexane	25	65	26	65
2-Methylpentane	73	93	74	91
3-Methylpentane	75	93	74	91
2,2-Dimethylbutane (neohexane)	92	106	93	113
2,3-Dimethylbutane (diisopropyl)	103	119	94	112
Pentene-1	91	99	77	83
2-Methylbutene-1	102	103	82	84
2-Methylbutene-2	97	99	85	86

The original application of isomerization was the World War II conversion of *n*-butane to *i*-butane for subsequent conversion to "alkylate" for aviation gasoline. A few pentane and hexane units also operated during the war to produce *i*-pentane and neohexane for blending into aviation gasoline. After the demand for aviation gasoline dropped with the end of the war, isomerization was of little interest until about 1955, when fast-rising octane ratings of motor gasolines revived interest in it.

To produce balanced gasolines of the proper volatilities, both light and heavy materials must be used. Without isomerization, the highest-octane light materials that are available in volume are light gasolines from catalytic cracking, which rate about 99 research octane number with 3 cc of tetraethyllead. As octane numbers rise, it is increasingly difficult to blend balanced premium gasolines with light catalytic gasolines as the volatile component (15,28), and isomerization of light virgin gasolines becomes economical, especially on a road octane basis (11,15,16). The first commercial isomerization units for the improvement of motor gasoline were announced in 1957.

Isomerization of olefins is of potential interest for upgrading olefinic synthetic gasolines of the future. Also, processes have been proposed for isomerizing alkyl aromatics (8,9,24) for the production of various chemical intermediates, such as *p*-xylene. During World War II, dimethylcyclopentanes were isomerized to methylcyclohexane for subsequent dehydrogenation to toluene (5,26). Because naphthenes are both isomerized and dehydrogenated in catalytic reforming (as discussed in Chap. 8), the separate isomerization of naphthenes is no longer of interest, at least as a method for making aromatics. Paraffin wax can be isomerized to low-pour-point lubricating oils (10), but no commercial applications have been reported.

Isomerization of Paraffins

Isomerization of paraffins requires the use of catalysts. There is little heat evolved, and reaction is limited by equilibrium and rate considerations. In the selection of conditions, side reactions must be taken into account.

Catalysts. Aluminum chloride was the wartime catalyst; it was used for isomerizing butane, pentane, and hexane feeds. In 1956, four supported-metal catalysts were announced for pentane and hexane feeds (18,20,22,29), and one was announced in 1958 for converting butane (13). Four of these are "noble-metal" catalysts, one is not. Three of the four noble-metal catalysts contain platinum. Other materials reported to be catalysts are molybdena on alumina (4,12) and nickel on silica-alumina (3).

Equilibriums and Rates. Isomerization equilibriums depend only on temperature. As determined experimentally, isomerization equilibriums are shown in Fig. 10-1 for butanes, pentanes,* and hexanes at temperatures up to 400°F. Because branching is reduced as temperatures are increased in each case, lower temperatures are preferred. However, reaction rates must also be considered. For the aluminum chloride

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* For pentanes, neopentane is favored thermodynamically, but none is formed experimentally (5,23).

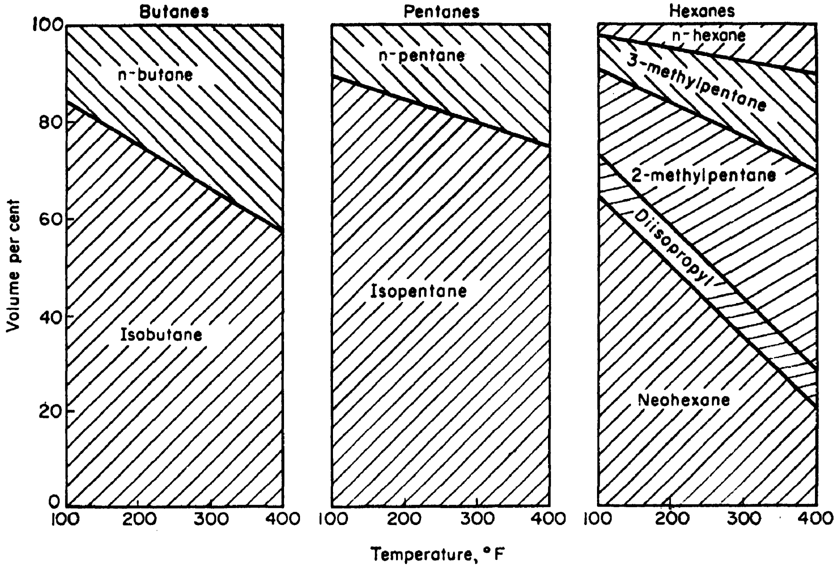

FIG. 10-1. Equilibrium compositions (14).

catalysts, which have high activities, temperatures of 180 to 300°F have been used (6). For the less active supported-metal catalysts, temperatures in the neighborhood of 700°F, or higher, are required. Thus, as shown in Fig. 10-2, the supported-metal catalysts are limited to lower octane levels than aluminum chloride catalysts, at least in once-through operations. The high-temperature equilibriums shown in this figure were calculated from heats of combustion; experimental results are less favorable (3).

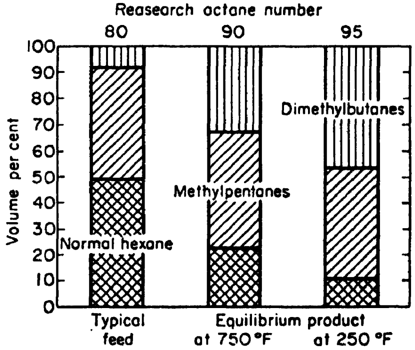

FIG. 10-2. Compositions and leaded octane ratings of hexanes (15).

Side Reactions. In the isomerization of butane, side reactions are almost negligible, but they are important in the processing of heavier hydrocarbons. With aluminum chloride catalysts, the principal side reactions are disproportionation to higher- and lower-molecular-weight materials (6). Disproportionation is suppressed by the addition of a small amount of benzene to the feed or by operating under a substantial pressure of hydrogen. By comparison with catalytic reforming, the principal side reactions with supported-metal catalysts can be presumed to be hydrocracking.* High hydrogen

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* For a discussion of hydrocracking in catalytic reforming, see Chap. 8.

pressures are used to suppress hydrocracking (27) and also to minimize the deposition of coke on the catalyst and thus permit long on-stream periods. The inclusion of 0.2 to 0.5 per cent benzene in the feed is also said to be beneficial in suppressing coke formation and other side reactions (27).

Because isomerization is limited by equilibrium considerations and side reactions are not, overtreating results in a loss in yield with no additional product improvement. To avoid unnecessary losses, reaction severity must be closely controlled.

Reaction Mechanism. Various theories have been proposed for the isomerization activity of aluminum chloride, but there is no general agreement as to the mechanism of reaction (23). Proposed mechanisms involve the formation of loose associations between the feed and catalyst, the formation of carbonium ions, or both (11,30).

The isomerization activities of supported-metal catalysts are associated with their acidities. It is postulated (2) that olefins are intermediates in the reaction, the olefins accepting protons from the catalyst to form carbonium ions that isomerize.

Low-temperature Processes

Seven processes have been operated for low-temperature isomerization of paraffins (6). In all of them the catalyst consists of aluminum chloride plus hydrogen chloride. As shown in Fig. 10-3, their general features are similar. Feed stock, dried and preheated to reaction temperature, is combined with a recycle stream (if recycling is practiced), mixed with hydrogen chloride, and passed through a reactor and an aluminum chloride recovery section. Reactor effluent is cooled and flashed to discharge any light gases through a small absorber (not shown) that recovers hydrogen chloride carried off in the gases. Liquid from the flash drum is stripped to recover hydrogen chloride, and is caustic-washed to remove the last traces of acid. The stripping column, which contains about 20 trays (6), is usually operated at a pressure high enough

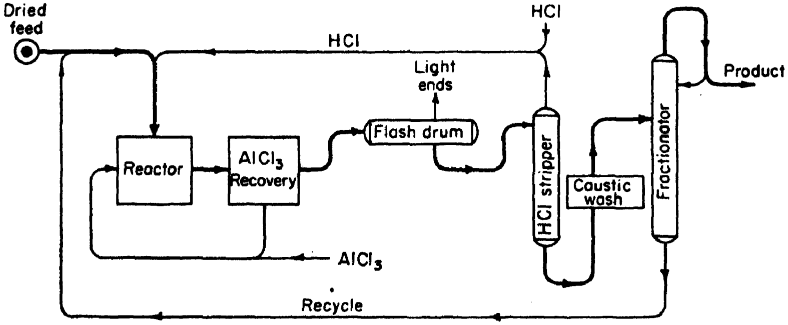

FIG. 10-3. Low-temperature isomerization unit.

that the stripped hydrogen chloride can be returned directly to the reactor. If recycling is practiced, the recycle stream is then fractionated from the product.

Aluminum chloride is volatile at commercial reaction temperatures, and is somewhat soluble in hydrocarbons (7); the various processes differ principally in the provisions used to prevent its migration from the reactor. For pentane and hexane processes, different methods are also used to inhibit side reactions.

Process data are shown in Table 10-2 for butane isomerization (6,14) and in Table 10-3 for pentane and hexane isomerization (6).

Table 10-2. Process Data for Butane Isomerization

Process	Vapor phase		Liquid phase		
	Shell	Anglo-Jersey	Universal Oil Products	Standard Oil Co. (Indiana)–Texas	Shell
Catalyst form	Impregnated bauxite	Sublimed on bauxite	Complex on quartz chips	Liquid complex	Dissolved in $SbCl_3$
Catalyst life, gal *i*-butane/lb $AlCl_3$	200	200	50–120	50–120	50–120
HCl concentration, wt %	2–14	4	5	4	5
Once-through conversion, %	40	35	38	38	45
Selectivity[a]	95	95	97	97	97
Reactor conditions:					
Temp., °F	210–300	270	200	205	180
Pressure, psi	200	235	235	365	300
Space velocity, vol/vol/hr	0.5–1.0	0.5–1.0	0.5	1.0	2.5

[a] $\text{Selectivity} = \dfrac{i\text{-butane produced}}{n\text{-butane converted}} \times 100$

Table 10-3. Process Data for Pentane and for Hexane Isomerization at Low Temperatures (6,15)

Process	Shell	Standard Oil Co. (Indiana)		
Feed	Pentane	Pentane	Pentane	Hexane
Inhibitor	H_2 (60 psi)	Bz (0.5%)	H_2 (60–180 scfb)	
Pressure, psi	300	300	700–850	800
Temperature, °F	176–212	180–210	200–250	250
Vol/hr/vol	2.5	1.0	....	1.4
HCl conc., wt %	5	5	....	8
Conversion, %	60	60	73	
Selectivity[a]	97	97		

[a] $\text{Selectivity} = \dfrac{i\text{-pentane produced}}{n\text{-pentane converted}} \times 100$

Vapor-phase Butane Isomerization (6). The first two butane-isomerization processes operated in the vapor phase, and, in both, the aluminum chloride catalyst was adsorbed on 4–20 mesh particles of a highly refined bauxite, Porocel, and thus its vapor pressure was reduced. Porocel was also used as a cleanup adsorbent for the reactor effluent, either in a separate chamber or in the upper section of the reactor. In the Shell Isocel process, the catalyst was preformed outside the reactor. In the Anglo-Jersey* process, aluminum chloride was sublimed onto the Porocel in place; this technique permitted the addition of aluminum chloride in the feed vapor to make up for deactivation of the catalyst during operation.

In both vapor-phase processes, it was necessary to shut the plant down periodically to change the catalyst. In the Isocel process, shutdowns resulted from loss in catalyst activity; in the Anglo-Jersey process, they resulted from building up the aluminum chloride content of the catalyst to the point that carry-over in the products became excessive.

Liquid-phase Butane Isomerization (6). Liquid-phase butane isomerization processes operate continuously; thus, they have a substantial advantage over vapor-phase operations. Of the three liquid-phase processes, two employ as catalyst a liquid complex made from aluminum chloride, hydrogen chloride, and hydrocarbons.† In the Universal Oil Products process, aluminum chloride is dissolved in the feed and the solution is passed down through a bed of quartz chips, together with hydrogen chloride. The catalyst complex, forming in the reactor, adheres to the chips. Thus, it passes through the reactor slowly, and it is substantially spent when it reaches the bottom, from which it is withdrawn and discarded. Some aluminum chloride passes through the reactor dissolved in the reactants. It is recovered by distillation, most of the reactor effluent being taken overhead. The aluminum chloride, recovered as a bottoms slurry, is recycled.

The Standard Oil Co. (Indiana)–Texas Company process also employs aluminum chloride–hydrocarbon complex, but simply as a pool of liquid,

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* The Anglo-Iranian Co., which participated in the development of the process, is now called the British Petroleum Corp. "Jersey" refers to the Standard Oil Co. (New Jersey).

† When aluminum chloride and hydrogen chloride are contacted with hydrocarbon, a liquid complex of aluminum chloride, hydrogen chloride, and hydrocarbon is formed. The complex is about as viscous as a heavy motor oil, has a specific gravity of 1.5, and is immiscible with liquid hydrocarbons. It is a good solvent for aluminum chloride, and its isomerization activity increases with aluminum chloride content. The range of desirable contents is narrow. At least 65 per cent aluminum chloride is desirable for isomerization activity. At 200°F, the distribution coefficient for aluminum chloride in hydrocarbons–aluminum chloride in complex increases sharply above 72 per cent. Thus, losses to the reactants increase sharply above a concentration of 72 per cent in the complex.

about 20 ft deep, through which the feed is bubbled. As in the Universal Oil Products (UOP) process, make-up aluminum chloride is dissolved in the feed. Because aluminum chloride is highly soluble in the complex, little is carried out in the reactor effluent, and an aluminum chloride recovery tower is not needed.

In the third liquid-phase process (Shell Oil Company), the aluminum chloride is employed as a 9 per cent solution in antimony trichloride. Because the catalyst solution is considerably denser than the reactants (its specific gravity is 2.5), a stirred reactor is used. Dissolved antimony trichloride and aluminum chloride are separated from the reactor effluent by distillation. An undesirable hydrocarbon–aluminum chloride complex forms during reaction and dissolves in the antimony trichloride. To hold the concentration of the hydrocarbon complex below about 3 per cent, a slip stream of the antimony trichloride solution is passed through an extraction tower countercurrent to the feed, which dissolves only the desirable materials. The undesirable complex is withdrawn from the bottom of the extractor and is discarded.

Pentane Isomerization (6). In general, the conditions for isomerizing pentane are similar to the conditions for butane, except that inhibitors are used to suppress side reactions. In the Shell Oil Company process, the catalyst consists of 2 per cent aluminum chloride dissolved in antimony trichloride, and a hydrogen pressure of 60 to 100 psi is used as a suppressant. Because increasing hydrogen pressures slow the isomerization reactions, the hydrogen pressure used is the minimum pressure that gives satisfactory catalyst life. In the Standard Oil Co. (Indiana) process, which employs a liquid catalyst complex, a small amount of benzene (0.25 to 0.5 per cent) constitutes the inhibitor. Make-up aluminum chloride is added as a slurry.

Hexane Isomerization (6,15). Because higher-boiling hydrocarbons are more prone to disproportionation reactions, a more effective inhibitor is required for hexanes. Hydrogen at high pressures (60 to 180 cu ft per bbl at 700 to 800 psi) is used. These high pressures preclude operation of the hydrogen chloride stripper at a pressure high enough to return the stripped hydrogen chloride directly to the reactor. Consequently, as shown in Fig. 10-4, the hydrogen chloride is absorbed in the feed at a lower pressure, and the rich solution is then pumped into the reactor. This arrangement also facilitates elimination from the system, as absorber off gas, light gases produced in the operation.

Once-through operations on a hexane fraction from a Mid-Continent crude yields 96 vol per cent of a debutanized product with a research octane number of 79 and a motor octane number of 78, both on an unleaded basis. Higher-octane products are made by separating a dimethylbutane concentrate by fractionation and recycling the remainder.

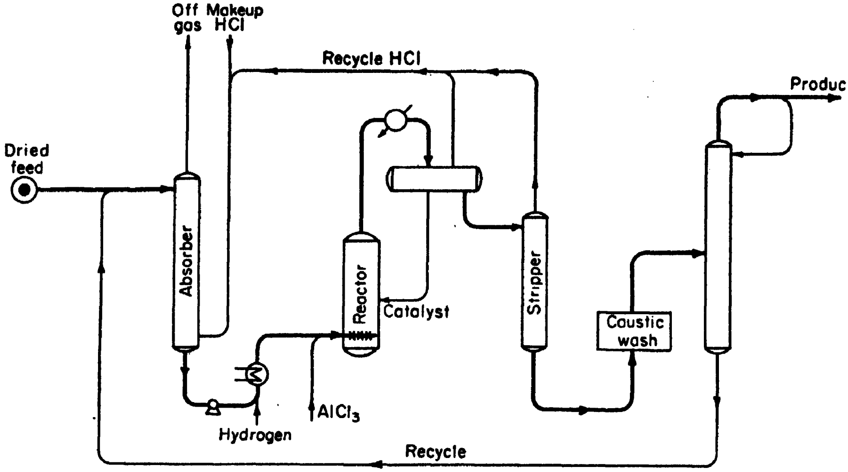

FIG. 10-4. Schematic low-temperature hexane-isomerization unit.

How recycling affects yields and product quality is shown in Fig. 10-5. In the recycling operation, a naphthenic concentrate is separated to prevent its building up in the recycle stream. Excluding the naphthenic concentrate from the product raises its octane rating by 0.5 to 2.5 units (6,15).

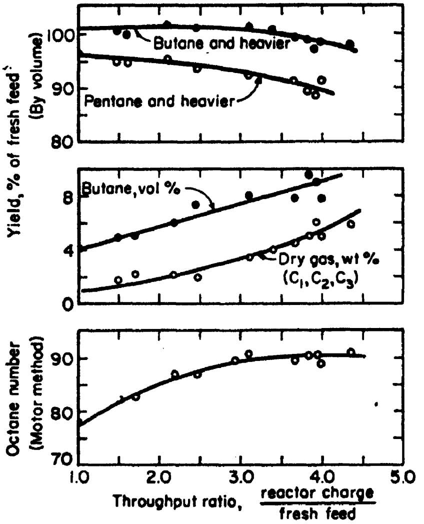

FIG. 10-5. Effects of recycling in low-temperature isomerization (5).

Feed Stocks (6). Because aluminum chloride is expensive, materials that react with it must be excluded from feed stocks. These include water, sulfur compounds, and olefins. In butane isomerization, heavy paraffins must also be minimized, inasmuch as an inhibitor is not used. For vapor-phase butane-isomerization units, which must be shut down to change catalyst, the recommended limits of reactable materials are 0.005 per cent water, 0.005 per cent sulfur, 0.1 per cent olefins, and 0.5 per cent pentanes. "Somewhat higher" levels are tolerable in liquid-phase butane units. In the isomerization of pentane, olefin concentrations as high as 0.2 per cent and hexane concentrations as high as 5 per cent are tolerable.

Operating Problems (6). The principal wartime operating problems resulted from the handling of aluminum chloride and hydrogen chloride.

Included among the problems were the plugging of reboilers in aluminum chloride recovery columns and hydrogen chloride strippers, the pumping of aluminum chloride slurries, and corrosion. Corrosion was particularly severe in the liquid-complex processes at points of high turbulence, high concentrations of hydrogen chloride, and high concentrations of free aluminum chloride.

The use of vertical thermosiphon reboilers designed for high circulation rates solved the reboiler problem (for aluminum chloride recovery columns at least), and satisfactory methods were found for pumping slurries. Presumably, the corrosion problems can be solved by choosing the proper materials of construction. One of the more promising wartime developments was the use of Lumnite cement linings. Hastelloy B is also satisfactory, but it is expensive.

High-temperature Processes*

Relatively little has been published on the high-temperature processes. In comparison with low-temperature processes, they have the advantage of avoiding the handling of aluminum chloride and hydrogen chloride. Balanced against this advantage are the less-favorable paraffin equilibriums at the higher operating temperatures required.

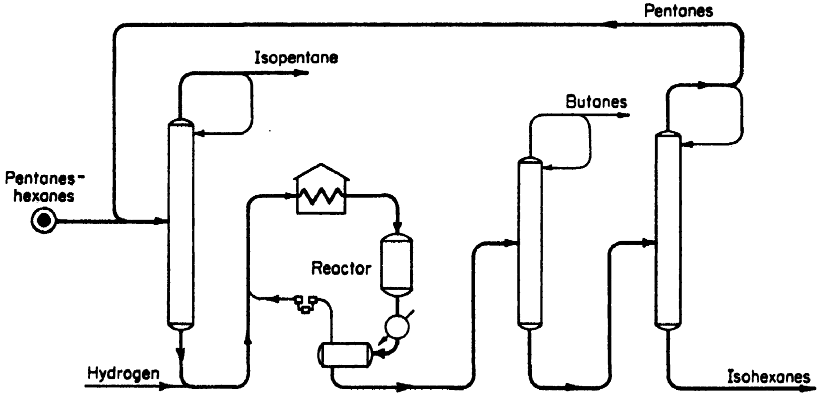

Fig. 10-6. Typical high-temperature isomerization unit.

As shown in Fig. 10-6, a high-temperature unit is similar to a catalytic reformer, except that a single reactor is used, inasmuch as the heat of reaction is small. Typically, a pentane-hexane feed, combined with a pentane recycle stream, is fractionated to take *i*-pentane overhead. The fractionator bottoms are mixed with hydrogen, preheated, and charged to the reactor. Reactor effluent is cooled and flashed to separate

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* High-temperature processes include Penex and Butamer (Universal Oil Products Co.), Pentafining (Atlantic Refining Co.), Isomerate (Pure Oil Co.), and Iso-Kel (M. W. Kellogg Co.).

recycle hydrogen from the product, which is stabilized and then depentanized, the pentanes being recycled to the deisopentanizer. *i*-Pentane and the *i*-hexane bottoms from the depentanizer constitute the product. Some improvement in yield can be obtained by charging pentane and hexane feeds to separate reaction systems and operating each at the conditions optimum for it (1).

When the feed *i*-hexane to *n*-hexane ratio exceeds 0.8, splitting the feed has been recommended to bypass the virgin *i*-hexanes around the isomerization reactor (11).

Process Data. Only sketchy process data have been published for high-temperature units, as shown in Table 10-4. Supported-metal catalysts are used in all processes, and temperatures in the range of 700 to 900°F and pressures of 300 to 750 psi have been reported for two of them. Operating results reported for the others indicate that they operate at the same conditions.

Table 10-4. Process Data for High-temperature Isomerization

Process	Butamer and Penex	Pentafining	Isomerate	Iso-Kel
Catalyst	Pt	Pt on SiAl	Non-noble metal	Precious metal
Temperature, °F	....	700–900	750	700–850
Pressure, psi	....	300–700	750	100–750
Space velocity, wt/hr/wt	....	1–6		
H_2 recycle, mole/mole	Yes	2–6	Yes	1–5
Halide promoter	....	None		
Regeneration	None	Steam-air	Infrequent	Regenerable

Hexanes isomerize more readily than pentanes. With a nickel catalyst, equal rates are obtained when hexanes are processed at a temperature about 70°F lower than pentanes (3). Together with the reported energy of activation (54 kcal per mole), this difference indicates that hexanes react about five times as fast as pentanes when both are processed under the same conditions. To minimize cracking reactions, hexanes are preferably processed at lower temperatures than pentanes.

Inasmuch as fixed-bed isomerization catalysts are similar to the catalysts used in catalytic reforming, it seems likely that they would respond similarly to trace elements in the feed, and "desulfurization of the feed stock to a low level" has been recommended (25). Nitrogen compounds also reduce isomerization rates over such catalysts (17), and they should probably be excluded from feeds. Catalysts supported on silica-alumina are claimed to be insensitive to nitrogen (29).

Yield-octane Data. Once-through results have been reported for butane, pentane, and hexane. About 40 per cent of *n*-butane is converted, with a volumetric *i*-butane yield of about 100 per cent (13). From *n*-pentane, yields of about 59 per cent *i*-pentane are reported, with only a 1 per cent loss to butane and lighter materials (11,16,29). Normal hexane can be converted to *i*-hexanes to the extent of about 70 per cent, with about 2 per cent loss to butane and lighter materials.

Results on refinery hexane feeds are shown in Table 10-5. Without prefractionation of the feed, all the product octane numbers range between 66.3 and 72.2 on a clear research basis, between 88.7 and 92.4 with 3 cc of TEL; the differences probably reflect differences in benzene and naphthene contents. Yields range between 94 and 98 vol per cent.

Table 10-5. Once-through Operations in High-temperature Isomerization of Hexane Feeds

	Without prefractionation				With prefractionation		
Feed:							
Research octane, clear	46.8	54.9	56.4	62.2	62.0	66.6	59.8
Research octane, with 3 cc TEL	78.0	82.2	83.3	87.5	85.0	89.4	85.6
Reid vapor pressure, lb	5.2	....	....	....	6.1	5.2	5.4
Product:[a]							
Yield, vol %	94.3	95.0	95.0	98.1	97.0	97.3	96.5
Research octane, clear	70.4	66.3	69.2	72.2	74.4	76.2	73.3
Research octane, with 3 cc TEL	91.8	88.7	90.7	92.4	93.8	95.0	93.3
Reid vapor pressure, lb	6.1	....	....	....	7.5	5.6	5.9
Increases:							
Research octane, clear	23.6	11.4	12.8	10.0	12.4	9.6	13.5
Research octane, with 3 cc TEL	13.8	6.5	7.4	4.9	8.8	5.6	7.7
Reference	(11)	(20)	(20)	(20)	(22)	(11)	(11)

[a] The products cited from reference 20 do not include the small amount of pentanes produced in isomerization of hexanes.

With prefractionation of the feed, product octane ratings are slightly higher.

Recycling of *n*-pentane is generally advantageous in higher-temperature units (18,19,20,22,29), but recycling of *n*-hexane probably is not (20), except when the *i*-hexane content of the feed is high enough to justify a feed deisohexanizer (16).

Isomerization of Olefins

Synthetic gasolines from Fischer-Tropsch operations contain large amounts of straight-chain olefins with terminal double bonds. The octane ratings of such gasolines can be improved as much as 20 units by vapor-phase isomerization over a synthetic cracking catalyst (6). At the present time, the process is of little commercial importance.

Investment and Operating Costs

Cost estimates have been published for pentane- and hexane-isomerization units, both for low-temperature and for high-temperature operations. Unfortunately, the basis is seldom clearly stated. Exceptions are for a Pentafiner, for Iso-Kel units, and for an Isomate unit.

For a high-temperature Pentafining unit that converts 2,000 bbl per day of 50 per cent *i*-pentane to 95 per cent *i*-pentane, the investment cost was quoted at $835,000 in 1956 (21). Only $235,000 of this cost was for the Pentafiner proper; the remaining $600,000 was for the associated pentane splitter. The estimated utilities are given in Table 10-6.

Table 10-6

	Pentafiner	Splitter	Total
Charge rate, bbl per day	1,783	3,758	
Fuel, 1,000,000 Btu per hr	7	53	60
Electricity, kw	65	213	278
Steam, lb per hr	1,600	0	1,600
Cooling water, gpm	30	128	158

The total direct operating cost, for a low-fuel-cost area, was quoted at 29.3 cents per bbl of charge.

A high-temperature Iso-Kel unit designed to charge 3,500 bbl per day of *n*-pentane was estimated at $1,475,000 in 1957 (16), including fractionation facilities. For a 3,100 bbl per day plant charging a pentanes-hexanes feed, investment was estimated at $1,100,000 without hexane recycle and at $1,425,000 with hexane recycle. Operating costs were quoted at 16 to 22 cents per bbl of feed. Product octane ratings for the mixed feeds were given as 96 and 96.7 research, with 3 cc of tetraethyllead.

For a low-temperature Isomate unit charging 5,000 bbl per day of pentanes-hexanes, in which *i*-pentane is first separated by fractionation and the remainder is processed once-through, investment costs were estimated at about 2 million dollars in 1957 (15). A typical product rates 96 to 98 research octane, leaded. If higher octanes are desired, methylpentanes and normal hexane are fractionated from the product and are put through the cycle again. Recycling raises the product octane to 101.8, but the investment is doubled. Estimated utilities are given in Table 10-7. With fuel at 13 cents per million Btu, operating costs were estimated at 25 cents per bbl for the once-through operation, 45 cents per bbl for the recycle operation.

Table 10-7

	Once-through	Recycle
Deisopentanizer feed, bbl per day	5,000	5,000
Reactor feed, bbl per day	4,040	6,710
Process heat, 1,000,000 Btu per hr	21.9	79.3
Electric power, kw	180	360
Cooling water, gpm	1,900	4,500

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CHAPTER 11

LUBE OIL, WAX, AND ASPHALT PROCESSES

Lubricating oils comprise less than 2 per cent of the petroleum products sold in the United States (19). Because their contribution to gross income is much higher, however, their manufacture is an important consideration in the economics of petroleum refining.

The principal function of lubricating oils is to provide a thin film of oil between sliding surfaces and thus to prevent wear and to minimize power losses. Also, the oil must flow freely enough to carry frictional heat away. Both of these properties depend upon the viscosity of the oil. Oils of the proper viscosity are found in the residual fractions of crudes—fractions higher-boiling than 600°F—and it is from these materials that most lubricating oils are made. Early lubricants, in fact, consisted simply of the crude-oil residuums having the most desirable properties.

In addition to normally liquid hydrocarbons, residuums may contain asphalt and wax. Both of these are undesirable in lubricating oils, and if present in appreciable quantities, they must be removed. Polycyclic structures are also undesirable in many applications, and they, too, must often be held to low concentrations.

Although asphalts and waxes are nuisances in lubricating oils, they constitute valuable by-products when separated. Because their production is linked with the production of lubricants, it is convenient to consider the manufacture of all three products together.

DEASPHALTING PROCESSES

Asphalts occur in petroleum in concentrations ranging from 0 to 65 per cent on crude (18). Their boiling points are in the range of the highest-boiling petroleum constituents, some of which are desirable materials for lubricating oils or for charging to catalytic cracking. Asphalts, however, oxidize readily and tend to form carbon and sludge; hence, they must be excluded from lubricating oils. Also, they are undesirable in feeds to catalytic cracking because they go largely to coke. Atmospheric distillation, acid treating, vacuum distillation, and propane deasphalting have been used commercially to separate asphalts from heavy stocks.

Atmospheric Distillation

The first deasphalting process was atmospheric distillation, which eliminates asphalt, but with poor recovery of potential lubricating oil or of charge to cracking. The boiling points of many of the good constituents are so high they would crack before they would vaporize, and such materials are left behind with the asphaltic residues.

Acid Treating

The next process to be adopted was acid treating (10), the universal panacea for refining problems at the time. Once applied generally to reduced crudes, acid treating is now in limited use. Its principal drawback is a considerable loss of hydrocarbon to sludge. Also the acid is costly, and disposal of acid sludge is difficult. Acid-treating techniques are described in Chap. 13.

Vacuum Distillation

The next innovation in deasphalting was distillation under vacuum, for example, at an absolute pressure of 40 mm Hg. Use of vacuum increases the amount of stock that can be vaporized below cracking temperatures. In the operation, two or more distillate fractions may be produced to provide base stocks of different viscosities for blending into lubricating oils. Typical yields and product inspections from processing the heaviest 38 per cent of a Mid-Continent crude are shown in Table 11-1. Although vacuum distillation improves yields substantially, it still leaves a good deal of desirable material in the asphaltic residue.

Table 11-1. Typical Yields from Vacuum Distillation

	Volume, per cent	Density, °API	Vis., SSU		Flash, °F	Color, NPA	Conradson carbon	Boiling range, °F at 1 mm Hg
			100°F	210°F				
Reduced crude	100	21	...	98	...	...	...	300+
Paraffin distillate	22	29	60	...	...	...	0	
SAE 10 cut	13	27	170	...	410	3	0	390–480
SAE 20 cut	19	24	520	60	475	4½	0.2	450–570
SAE 40 cut	13	21	...	100	545	...	0.8	520–630
Asphaltic bottoms	33	13	...	...	655			

To minimize cracking, one refiner employs a two-column vacuum unit, in which temperatures are held below 700°F (38). Only one distillate fraction is taken off in the first column, and it is separated into three fractions in the second. The bottoms from the first column are sent to a propane-fractionation unit (described below) to recover heavier lubricating oils.

Propane Deasphalting

The most recently developed deasphalting process, and the most selective, is propane deasphalting.* Near its critical temperature, propane dissolves hydrocarbons, while rejecting asphaltic materials (13).† Also, it dissolves smaller molecules in preference to larger ones (40). In the range of conditions used, raising the temperature of propane reduces its dissolving capacity and improves its selectivity. Increasing the propane-to-oil ratio increases the sharpness of the separation (22).

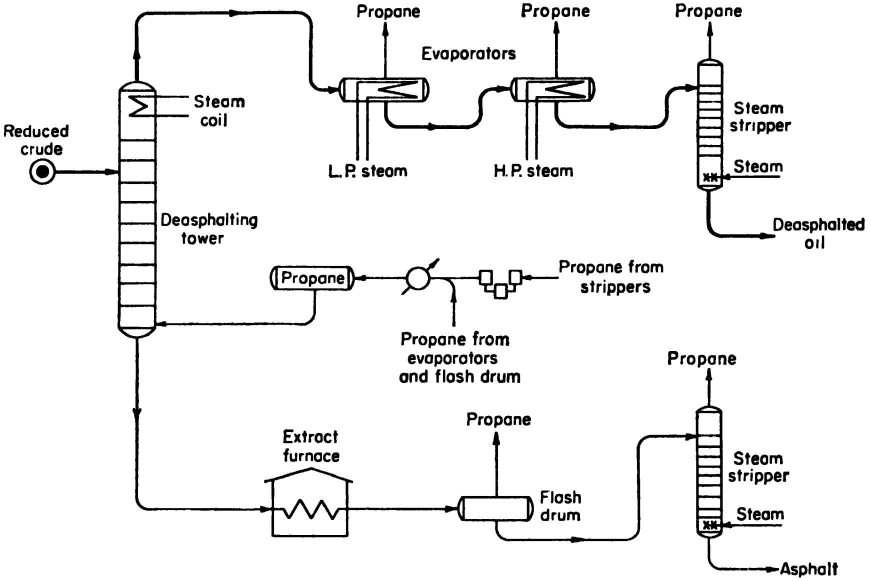

FIG. 11-1. Propane deasphalting.

A schematic flow diagram for a propane-deasphalting plant is shown in Fig. 11-1. Reduced crude is fed near the top of a liquid-liquid con-

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* The Duo-Sol process also employs propane in conjunction with another solvent to reject asphalt from lubricating stocks. However, the Duo-Sol process also extracts polycyclic aromatics, and it is generally classified as a solvent-extraction process.

† Asphaltic compounds in reduced crudes are believed to be colloidally suspended solids or semisolids. The addition of propane depeptizes them and permits them to separate.

tacting column, liquid propane at the bottom (10). The propane passes up the column, dissolving the oil and carrying it overhead; asphaltic materials pass out the bottom. The top of the column is heated by steam coils to reduce the oil-carrying capacity of the propane. As a result, some oil "refluxes" down the column to improve the sharpness of separation. Some propane is dissolved in the reject asphalt--perhaps one volume per volume (38). Propane is separated from the deasphalted oil and from the asphalt product by evaporation and steam stripping, the propane being condensed and recycled. Propane losses range from 0.1 to 0.5 per cent of the circulation rate (11).

Four to twelve volumes of propane are circulated per volume of oil charged (10,22). Column temperatures range from 100 to 130°F at the bottom and from 150 to 180°F at the top. The column, which is usually 40 ft tall or taller, is held at a pressure high enough to keep the propane liquid; pressures range up to 550 psi. One column is reported to contain 16 perforated trays and to charge 9.6 cu ft of oil per hr per sq ft of column cross section (27). Holding the oil-propane interface low in the column is indicated to give smoother operations (38). Typical yields for propane deasphalting are shown in Table 11-2.

Table 11-2. Typical Propane-deasphalting Yields (37)

	Source of crude				
	Oklahoma	Iraq	Le Duc	Illinois	Pennsylvania
Reduced crude:					
Gravity, °API	19.3	7.1	12.1	13.7	25.1
Viscosity, SSU at 210°F	385	4880	2050	1760	220
Conradson carbon, wt %	7.3	19.7	17.1	13.4	2.8
Deasphalted oil:					
Yield, vol %	75.6	34.1	47.1	50.7	83.7
Gravity, °API	23.6	20.2	22.7	23.4	26.6
Viscosity, SSU at 210°F	141	179	199	190	144
Conradson carbon, wt %	1.5	2.4	1.7	1.4	1.1
Asphalt:					
Yield, vol %	24.4	65.9	52.9	49.3	16.3[a]
Specific gravity	1.023	1.064	1.054	1.030	0.953[a]
Softening point, °F	144	145	176	145	
Solvent-oil ratio used	7.8	9.9	7.9	8.0	12.7

[a] Resins.

At somewhat higher deasphalting temperatures (for example, 190°F at the column top), the heaviest lubricating stock or "bright stock" is rejected with the asphalt bottoms (38). The bottoms can then be charged to a second column operating at the usual conditions to separate bright stock from asphalt. Because such an operation separates the potential lubricating oil into two fractions, it is called "propane fractionation" (37,38).

MANUFACTURE OF ASPHALTS

Petroleum asphalts are prepared directly by vacuum distillation or by propane deasphalting, and also by distillation followed by air-blowing the bottoms to convert aromatic hydrocarbons into asphaltenes (1,32). Residual asphalts are often preferred for paving, blown asphalts for roofing (18). How two of the important properties of residual and blown asphalts compare is illustrated in Fig. 11-2, which plots consistency (measured in a penetration test) against pliability (measured in a ring-and-ball softening test). The upper curve indicates how the properties of a residuum change as it is blown with air. The lower curve shows how the properties change if the residuum is further reduced by distillation. If asphalt properties between the curves are desired, they can be obtained by reducing the residuum to the proper point and then air blowing, as shown by the intermediate curve. Asphalt properties above the top curve can be obtained by air blowing in the presence of catalysts such as ferric chloride and phosphorus pentoxide (18).

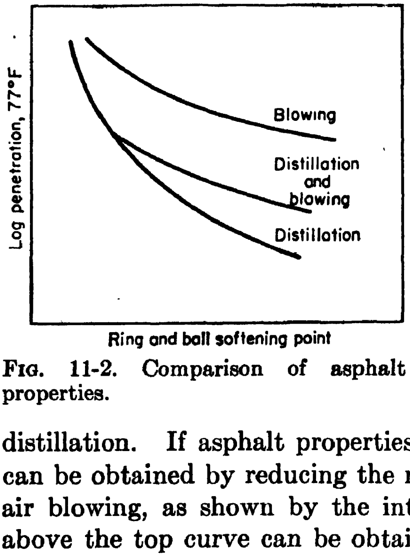

FIG. 11-2. Comparison of asphalt properties.

In preparing residual asphalts, it is usually important to avoid cracking conditions, which would prevent the product from meeting the Oliensis test.* In modern vacuum units, distillation temperatures as high as 800°F may be permissible (15).

Blowing is usually carried out batchwise in stills equipped to blanket the charge with steam (18). Air is passed through the charge at 400 to 500°F at the rate of about 40 cu ft per min per ton of charge until the desired hardness is attained. The reaction consists principally of dehydrogenation followed by polymerization or condensation (12,18). (Most of the oxygen is converted to water.) No heat is required, since

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* For some uses, asphalts from cracked stocks are believed to be inferior to asphalts from virgin stocks. The Oliensis test is intended to differentiate between virgin and cracked asphalts. However, some virgin stocks fail to pass the test.

the reaction is exothermic. Yields may range from about 97 to about 99 per cent of the charge. Blowing a Mid-Continent residue for 8 hr raised its softening point from 100 to 230°F, with a yield of 99 per cent (15).

Blowing is also done continuously by pumping the charge through a preheating furnace and then through a column through which air is passed countercurrently. Steam is often charged with the air to control the temperature, and product recycle is employed as needed to attain the desired product qualities (18).

Since sludges from acid treating of reduced crudes are rich in asphalt, it might be expected that asphalts could be produced from them. Asphalts have been made from heavy-oil sludges by a combination of air blowing and steaming, but the products were inferior (16).

DEWAXING PROCESSES

Petroleum waxes are hydrocarbons which are solids at ordinary temperatures, with melting points usually in the range of 90 to 200°F. They are soluble in other hydrocarbons, and, in their natural state, they are dissolved in crude oils. Petroleum waxes boil in the temperature range of lubricating oils and cannot be separated from them by distillation. Because they crystallize out at low temperatures, waxes are undesirable in motor oils and often must be removed.* Thus, they are usually produced as by-products of the manufacture of motor oils.

Waxes are classified according to their physical forms. Those that crystallize in the form of large crystals are called paraffin (or crystalline) waxes, and those that form very small crystals are called microcrystalline (or amorphous). Paraffin waxes are obtained from light lubricating-oil fractions. Heavier stocks yield microcrystalline waxes.

Paraffin waxes consist largely of normal paraffins, but they may contain as much as 35 per cent of other materials, principally *i*-paraffins and monocycloparaffins (8). The non-normals predominate in the heavier cuts, which suggests that still heavier waxes are microcrystalline because they contain more non-normal material.

The same property of waxes that makes them a nuisance in lubricating stocks permits them to be removed. The oils are first chilled by refrigeration to crystallize the waxes, which are then separated by filtering, centrifuging, or settling. Chilling is usually accomplished by pumping the waxy charge through the inner tubes of double-pipe exchangers,

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* Certain chemicals inhibit the crystallization of wax. These materials, called pour-point depressants, are sometimes added to oils. The addition of 0.06 per cent of one such material reduced the pour point of a Mid-Continent oil from +20 to −15°F (25).

the inner tubes being equipped with helical scrapers to prevent the build-up of wax in the tubes (30). In modern processes, dewaxing is carried out with the help of selective solvents (10,24), which dissolve oil but reject wax and thus give sharper separations of wax from oil. In 1955, 86 per cent of the dewaxing operations employed solvents (29).

Petroleum oils can also be dewaxed without refrigeration by the use of urea, which forms crystalline addition compounds with straight-chain hydrocarbons at atmospheric temperatures (5,36).

The viscosity of dissolved wax is lower than that of the oil with which it is associated. Consequently, dewaxing raises the viscosity of an oil somewhat (23), and the viscosity index is usually lowered slightly.

Dewaxing without Solvents

Dewaxing was first accomplished by permitting wax-bearing oils to stand in tankage through the winter. As the oil cooled, some wax crystallized out and slowly settled to the bottom. These operations developed eventually into batch "cold-settling" processes, in which the chilling was done artificially, and naphtha diluents [about two volumes per volume of charge (17,23,30)] were used to speed the settling. Charge stocks were either heavy lubricating-oil distillates or reduced crudes, and the wax product was microcrystalline. Because long cooling and settling times were required,* tankage requirements were large. Subsequently, they were reduced somewhat by the substitution of centrifuging (30) for settling. To prevent sticking of the microcrystalline wax to the bowl of a centrifuge, either cold brine or hot water may be added to the centrifuge charge. Both are heavier than the wax product, and thus either forms an aqueous film on the inside of the whirling metal bowl. Centrifuging temperatures are usually in the range of −40°F (17), and the pour point of the product is about 40°F higher than the temperature of operation (17,23,30).

Cold-settling or centrifuging processes will not work on the lighter lubricating-oil stocks because the paraffin-wax particles that are formed cannot be settled or centrifuged out of the chilled oils. However, paraffin waxes are crystalline, and they can be filtered out. "Cold pressing," which had been developed previously for dewaxing shale oils, was adapted to this service. In carrying out the process, some gas oil lighter than lubricating oils is included in the charge to reduce its viscosity and to increase the yield of wax. Typical charge stocks boil between 300 and 600°F at 10 mm absolute pressure (10).

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* The recommended rate of cooling is 3 to 4°F per hr, at least down to 0°F (30). To avoid fouling of the cooling surfaces, the cooling medium should be less than 20°F cooler than the oil.

Filtration is carried out on plate-and-frame filter presses* under pressures as high as 500 psi (18). Wax is removed from the presses by hand. Because filterable wax—usually 5 to 15 per cent on charge—is paraffin wax, the charge to the operation became known as "paraffin distillate." For satisfactory filtration, a paraffin distillate must have a low viscosity, say 70 to 100 SSU at 100°F (10). Paraffin distillates of higher viscosity are sometimes diluted with naphtha to reduce viscosity, and the diluted charges are filtered; the diluent is then fractionated from the dewaxed oil. Filtration temperatures are usually about 0°F. When the gas-oil portion of the feed is fractionated from the dewaxed oil, any residual wax is concentrated in the lubricating-oil product. Consequently, the pour point† of the product is about 15°F higher than the filtration temperature (17).

Just as cold settling will not work on paraffin waxes, so also cold pressing will not work on microcrystalline waxes. Such waxes either plug up the filter cloths or pass right through (18). Consequently, both pressing and settling were required formerly if a full range of lubricating oils was to be produced. To ensure that microcrystalline wax was excluded from the filters and that paraffin wax was not charged to cold settling, a "slop cut" between the light charge to pressing and the heavy charge to cold settling was usually discarded (10). About 1928, a pressing process was developed that is applicable to any wax-bearing stock. This process employs a filter aid, such as diatomaceous earth, to build up the wax crystal structure (23). Its development was untimely, however, in that solvent processes that proved to be more economic were perfected about the same time (10). Only three commercial units were built to use the filter-aid process.

Dewaxing with Solvents

Broadly, naphtha could be considered the first solvent used in dewaxing, because it was added to certain charge stocks to facilitate the separation of waxes from oils. In general usage, however, naphtha is considered a diluent rather than a solvent. The use of more selective solvents was investigated as early as 1862, and three patents had been granted by

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* Plate-and-frame filters (30) consist of square vertical "plates" separated by "frames" to form cells, typically about 48 in. square by about ½ in. thick. There are depressions in the plates through which liquids may flow. Filter cloths are stretched across each plate surface. Slurries are pumped into the cells under pressure. The liquid passes through the filter cloths, flows down the channels formed by the depressions on the plates, and is taken off through a common liquid outlet. A single filter is made up of as many as five hundred cells.

† Pour point is the highest temperature at which the oil in a standard jar will not move when the jar is held in a horizontal position for 5 sec.

1914 (10). These early processes were not commercialized, probably because there was not an adequate supply of the special solvents required and because construction techniques were not good enough to hold losses of the expensive solvents to reasonably low levels. When a number of solvents became available commercially about 1925, investigation of solvent dewaxing was intensified, and the first commercial plant went on stream in 1927. This plant employed a mixture of acetone and benzene as solvent, for which a mixture of methylethylketone and aromatics was later substituted.* Although other solvent processes have since been developed, the term "solvent dewaxing" is usually reserved for this first one, which is also called the "MEK process." Others include the Bari-Sol, Separator-Nobel, and Edeleanu processes, and propane dewaxing (10). Of these, only propane dewaxing appears to be competitive with solvent dewaxing.

A major advantage for solvent processes over the earlier dewaxing methods is their applicability to all wax-bearing stocks; only one dewaxing plant is required, and no "slop cut" need be discarded.

Solvent (MEK) Dewaxing.† Solvent (methylethylketone) dewaxing is the process most widely used. Each of the two components of the solvent has a specific function. The ketone causes the wax to solidify in a crystalline, easily filterable form, while the aromatic component increases the capacity of the solvent for dissolving oil (17,23). Benzene-toluene mixtures are used as the aromatic material, more toluene being used when operating temperatures are low, because toluene has a lower freezing point than benzene.

A typical MEK plant is diagrammed in Fig. 11-3. The wax-bearing charge is mixed with the solvent and the mixture is chilled to crystallize the wax.‡ Chilling is accomplished in scraped-tube heat exchangers, first by exchange with the cold product and then with a refrigerant. The chilled feed is then filtered continuously on rotary vacuum filters (22) to separate the crystallized wax from the oil-solvent solution. While still on the filter, the wax cake is washed with solvent to displace retained oil. Filtered solution, including the washings, is heated to flash off the solvent, which is condensed and recycled. Oil from the

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* Acetone-benzene is easier to separate from the products, but it cannot lower pour points as far as does methylethylketone. Acetone-benzene is used in Greece, where pour points of 10°F are satisfactory (26*a*).

† Solvent dewaxing was developed by the Indian Refining Company and The Texas Company (10).

‡ The size of the wax crystals, and thus the filterability of the wax, depends among other things, on the viscosity of the solution from which the wax crystallizes and on the rate of cooling (30). To facilitate crystallization in an easily filterable form, the solvent may be added to the feed stagewise at two or more points in the chilling sequence (10,21,26*a*,37).

flashing operation still contains traces of solvent, which are stripped out in a steam-stripping tower.

The wax cake contains all the original water content as ice and also some solvent. The cake is melted (equipment not shown) and charged to a settling drum where melted wax and water separate, solvent distributing between them. Dilute solvent from the oil stripper is also charged to the settling drum, some of its solvent passing into the melted wax. The aqueous phase from the drum is fractionated to reject water as bottoms, the overhead being recycled to the drum to recover its solvent content by transfer to the melted wax. Melted wax from the drum is sent to an evaporator and a steam stripper. Solvent from the evaporator is relatively dry and is returned to the warm solvent stream. Dilute solvent from the wax stripper is sent back to the wax settling drum.

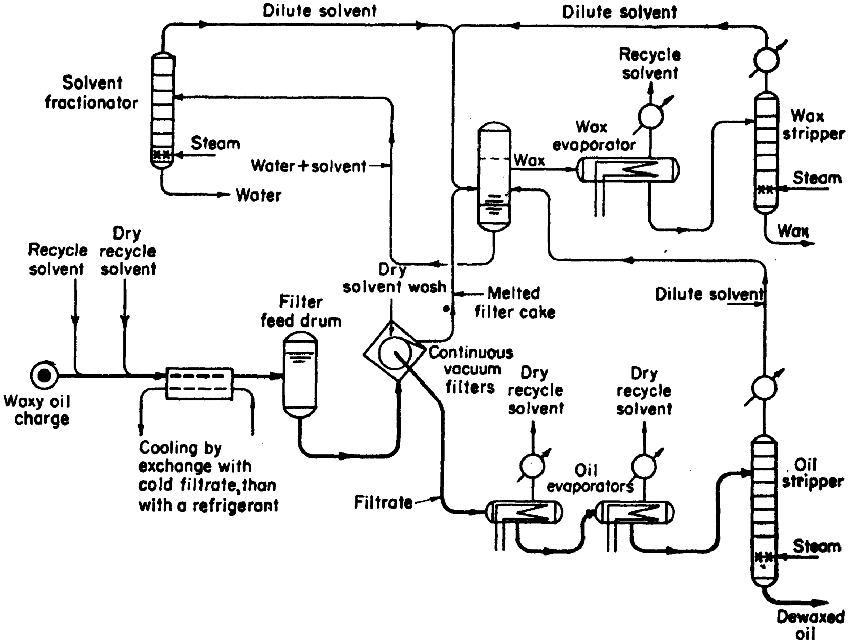

FIG. 11-3. MEK (solvent) dewaxing.

Filters require periodic washing with hot solvent to remove materials that plug the cloths. Sometimes, the plant is instrumented to take a filter off stream and to wash it automatically whenever the charge rate to it drops below a preset value (2).

MEK dewaxing is operated "at or a few degrees below" the pour point desired for the product oil and with solvent-charge ratios ranging from 1:1 to 4:1 (37). Chilling rates may be 30 to 100°F per hr (23). Operations reported for one plant are shown in Table 11-3.

Table 11-3. Solvent-dewaxing Operations (28)

	Feed stocks			
	Paraffin distillate	Light motor oil	Intermediate motor oil	Heavy motor oil
Viscosity of feed:				
SSU, 100°F	150	250		
SSU, 210°F	.....	.....	77	205
Operating conditions:				
Solvent/oil, vol/vol	1.9	1.7	2.2	3.2
Filtration temperature, °F	20	12	16	25
Filtration rate, gal/(hr)(sq ft)	6.0	6.3	4.2	2.8
Dewaxed oil:				
Yield, vol %	89	90	91	92
Pour point, °F	20	5	0	25
Ketone content, wt %	0.001	0.003	0.003	0.002
Wax:				
Yield, vol %	11	10	9	8
Oil content, vol %	7	5	8	12
Ketone content, wt %	.....	.....	0.001	0.001

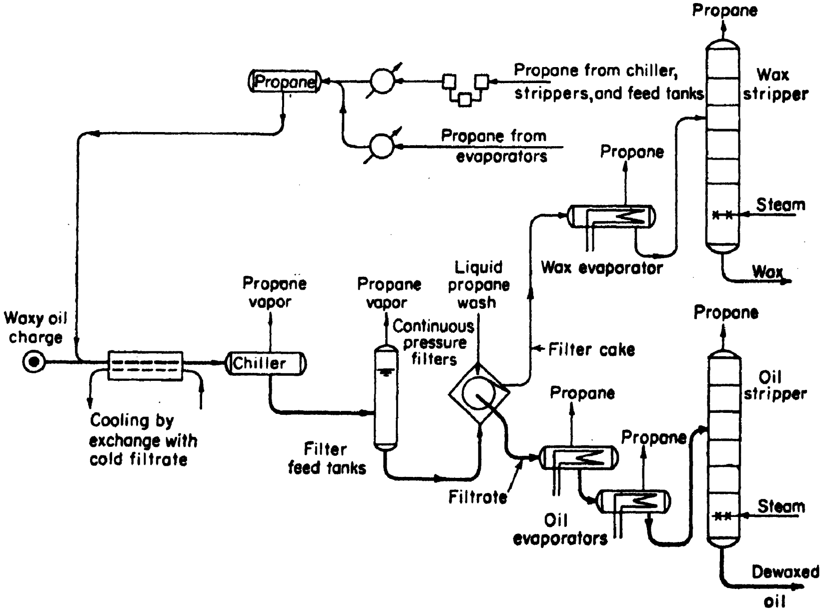

FIG. 11-4. Propane dewaxing.

Propane Dewaxing.* As shown in Fig. 11-4, a propane-dewaxing unit is very similar to an MEK plant. Aside from the solvent used, the principal differences are that the final chilling is done batchwise in propane dewaxing, that the propane itself is used as the refrigerant by permitting it to vaporize from the solvent-charge mixture at a controlled rate, and that propane dewaxing requires a temperature 20 to 30°F lower than the MEK process (10,23). The solvent-oil ratio is usually in the range of 1:1 to 3:1.

Automatic control of the batch-chilling operation increases plant capacity and improves the uniformity of the product (3).

Urea Dewaxing

The newest dewaxing process makes use of the fact that urea forms solid, filterable complexes or adducts with large paraffinic hydrocarbons that have little or no branching (3,9,26,39). This selectivity results from the dimensions of the various hydrocarbons; only straight chains can fit inside the channel formed by crystallizing urea. About 0.7 mole of urea is required for each carbon atom, or about 3 lb per lb of hydrocarbon. For adduction to be completed in a reasonable time, an activator, such as methanol, must be used. The time required, which increases with the size of the hydrocarbons, ranges from a few minutes to an hour or more (39). Decomposition of the adduct is accomplished by dissolving the urea in a suitable solvent or by heating it to about 200°F. Use of a solvent, such as water, has been recommended to avoid decomposition of urea (20).

Table 11-4

Charge		Liquid wax		Dewaxed oil	
SSU (100°F)	Pour point, °F	Per cent	Pour point, °F	Per cent	Pour point, °F
50	15	10	75	90	−55
80	35	7	60	93	−40
220	0	4	80	96	−25

Urea dewaxing is advantageous for the production of low-cold-test oils from light oils that contain small amounts of wax, for example, from solvent-dewaxed oils. Typical results are given in Table 11-4 (39). Because the wax in lower-viscosity oils contains a higher percentage of straight-chain hydrocarbons (8), urea dewaxing is more effective on

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* Propane dewaxing was developed by Standard Oil Co. (Indiana), Standard Oil Co. (New Jersey), Union Oil Co., and M. W. Kellogg Co.

lighter stocks. Its applicability to lubricating-oil distillates, without prior dewaxing, is questionable (12*a*).

A schematic flow sheet for urea dewaxing is shown in Fig. 11-5. Investment cost for a 1,000 bbl per day plant was estimated at $850,000 in 1957; operating costs at 2.2 cents per gal (39).

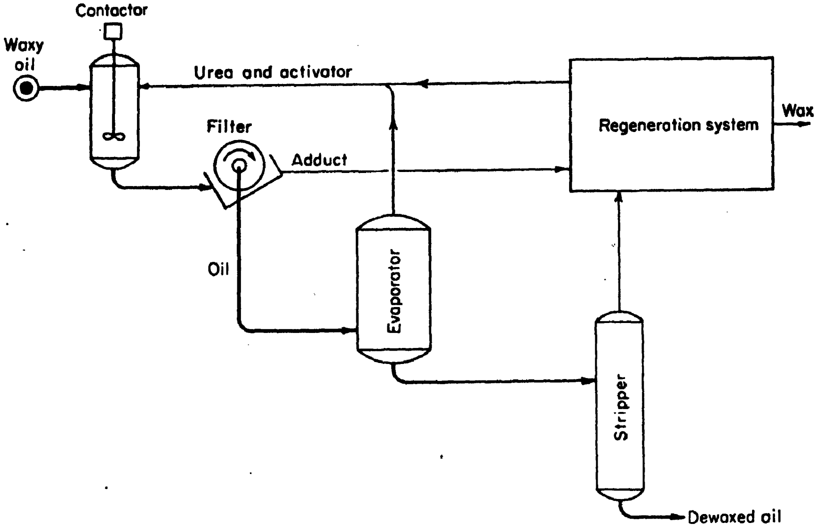

FIG. 11-5. Urea extraction.

DEOILING

The crude waxes produced in dewaxing operations contain from about 10 per cent to about 50 per cent oil, the lower oil contents resulting from dewaxing operations employing selective solvents. Except for petrolatums* the oil content often must be reduced below 0.5 per cent, and sometimes below 0.1 per cent, if the wax is to be made into a finished product (41). Originally, two types of processes were employed to effect this reduction—"sweating" for paraffin waxes and "resettling" or centrifuging for microcrystalline waxes. Considerable wax is still made by these methods. Modern units employ selective solvents.

Sweating

Sweating operations are conducted batchwise. Crude paraffin wax, often called "slack wax," is first melted and then cast into sheets,

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* Crude petrolatums are obtained in the dewaxing of low-asphalt (or deasphalted) reduced crudes. The dewaxed oils have viscosities of at least 125 SSU at 210°F and pour points of 0 to 15°F. Crude petrolatums contain about one-third microcrystalline wax, one-third resins, and one-third oil. They are finished by drastic clay percolation to improve color, odor, and taste. The clay treatment removes resins.

typically 10 ft by 40 ft by 4 in. thick (17). The casting is accomplished by pumping the melted wax onto a water surface in pans equipped with perforated false bottoms and then cooling by circulating cold water. After the wax has solidified,* the water is drawn off to drop the wax cake to the perforated false bottoms of the pans, which are arranged in vertical stacks in a single oven, with spaces for air circulation around each pan. The temperature in the oven is raised slowly—1 to 2°F per hr—by means of heating coils in the oven. As the temperature rises, some of the wax cake melts, and a mixture of oil and low-melting wax drains out and is withdrawn. Heating is continued until the remaining wax has the desired melting point. The reduction of oil content achieved in this operation may not be good enough, and the whole process may be repeated one or more times (17). The wax from the first sweating is called "crude scale wax," and it may contain 1 to 6 per cent oil (41). The oil-wax mixtures sweated out are called "drips," or "foots oil"; these may be reprocessed for the recovery of low-melting-point waxes, or they may be recycled back to the original sweating operations (30,41).

The recovery of finished wax from slack wax depends in large measure on its oil content. In one case, a slack wax containing 20 per cent oil yielded about 50 per cent crude scale, while little was recoverable from a slack wax containing 50 per cent oil (4).

Resettling and Centrifuging

Crude microcrystalline waxes were deoiled originally, and sometimes still are, by diluting them with cold naphthas, chilling the mixtures, and separating the wax products by settling or centrifuging the chilled solutions. This process, which may have to be repeated as many as four times, is usually operated in conjunction with a dewaxing plant that employs a naphtha diluent. In such a case, naphtha need not be separated from the charge to deoiling, and the naphtha-oil mixture settled or centrifuged from the wax may be returned to the dewaxing plant.

Deoiling with Solvents

Dewaxing is improved by substituting selective solvents for dilution naphtha. In addition to making the process applicable to all wax concentrates, selective solvents also give better separations. The use of a solvent for deoiling is particularly attractive in conjunction with a dewaxing plant employing the same solvent. In this case, as in naphtha-dilution plants, it is not necessary to separate solvent from the slack wax charged to deoiling.

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* Although paraffin slack wax is produced in the form of platelike crystals, the resolidified wax is in the form of needles of a type which permit oil to drain through the wax cake.

Either propane (30) or a mixture of MEK and an aromatic can be used for deoiling. The schematic diagram for either process is very similar to the diagram for a dewaxing plant employing the same solvent, except that slack wax (repulped in fresh solvent) constitutes the feed stock. With methylethylketone, deoiling is carried out at temperatures in the range of 5 to 60°F. Over-all solvent requirements for dewaxing and deoiling range from about 2.5 to 9 vol of solvent per volume of oil charged (35).

In one German plant, slack wax containing 5 to 10 per cent oil is first spray-dried to a powder that is dry, even though each particle is covered by a thin oil film (9*a*). The powder is then contacted countercurrently with a solvent (dichloroethane) in a two-stage mixer-settler system. Oil and low-melting-point wax are dissolved to yield waxes containing 0.2 to 0.5 per cent oil. Three to six volumes of solvent are used per volume of charge at extraction temperatures of 40 to 60°F.

WAX FINISHING

Waxes are often treated with sulfuric acid and with clay to improve color, odor, and taste. If propane dewaxing and deoiling are practiced, the acid and clay treating may be carried out in propane solution. Because of the lower viscosity of the propane solution, the separations of spent acid and of clay are simplified. Also, acid and clay requirements are reduced. Hydrogen treating is also used in place of acid and clay treating. Acid, clay, and hydrogen treating are discussed in Chap. 13.

SOLVENT-EXTRACTION PROCESSES*

Polycyclic materials are undesirable in lubricating oils, particularly in motor oils, because of their low viscosity indexes. An oil rich in polycyclic naphthenes is unsuitable for the production of motor oils. Polycyclic aromatics, however, can be removed by any one of several extraction processes, including the furfural, phenol, Duo-Sol, Edeleanu, Chlorex, and nitrobenzene processes. Basically all of these are similar. Each consists of facilities to contact the oil with a selective solvent that extracts the undesirable polycyclic aromatics, plus facilities to separate solvent from the extract and raffinate streams. The solvent must be vaporized on every circuit through the system. As large amounts of solvent are circulated, the heat requirements are high; they constitute one of the major operating expenses. Extraction equipment proper is

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* A general discussion of solvent extraction is given in Chap. 4.

relatively simple, but the solvent-recovery facilities are complex and therefore expensive.

Solvent extraction was introduced about 1930. As shown in Fig. 11-61 its use has grown rapidly. In 1955, 95 per cent of the lubricating oi, produced in the United States was solvent-extracted (34). The furfural, phenol, and Duo-Sol processes have proved to be the most popular.

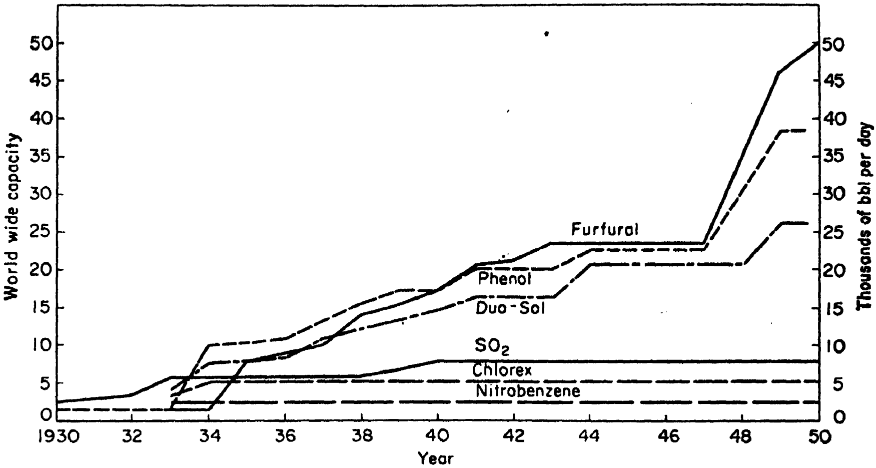

FIG. 11-6. Growth of lubricating-oil extraction.

Although the principal function of these processes is to improve viscosity index, they also remove materials which tend to oxidize, to impart color, or to form carbon under conditions of use. Deep extraction may also remove natural corrosion inhibitors (38).

General Relationships. Increasing temperatures increase the capacity, but reduce the selectivity of a solvent. Increasing the number of countercurrent contacting stages improves both the apparent capacity and selectivity, as illustrated in Table 11-5 for a Mid-Continent oil extracted with 200 per cent of furfural at 200°F (22). Conflicting estimates have been published for the number of stages used com-

Table 11-5

Number of stages	Raffinate	
	Yield, vol %	Viscosity index
1	78.0	84.5
3	73.5	87.0
5	71.5	88.5
7	70.0	89.5

mercially, for example, 1.4 to 4.0 by one authority (11), 3 to 8 or more by another (22). Both authors agree, however, that all commercial solvents give the same over-all results in terms of product quality-yield relationships. Typically, viscosity-index improvement is numerically equal to treating loss in per cent (31). With naphthenic feeds, the loss may be half as great; with high viscosity-index feeds it may be twice as great.

Furfural Extraction.* Furfural has proved to be the most popular solvent. It is stable (6,7), nontoxic, relatively cheap, and readily available. Furfural is selective at higher temperatures than are other solvents. Consequently, it has two advantages. Liquids are less viscous at higher temperatures and contacting of the feed and solvent is facilitated. Also, waxy stocks may be processed without difficulty. Because the selectivity of furfural is destroyed by water, the circulating solvent must be dehydrated continuously (11).

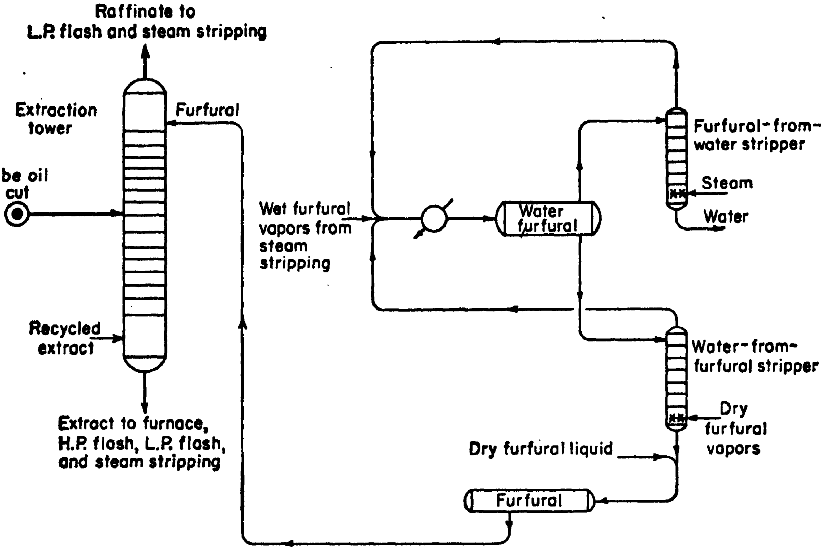

FIG. 11-7. Furfural extraction.

A schematic flow diagram for a furfural-extraction plant is shown in Fig. 11-7. Feed stock is charged to the middle of an extraction column and passes up, countercurrent to the solvent, which is introduced at the top. Downflowing solvent selectively extracts polycyclic aromatics together with some desirable stock. At and below the feed inlet, desirable materials are displaced from the furfural by a rising reflux stream, part of which is induced by charging the feed at a relatively low temperature to cool the solvent and thus reduce its carrying capacity. Recycle

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* Furfural extraction was developed by the Texaco Development Co.

extract, brought in at the bottom of the tower, provides the rest of the reflux. The bottom furfural-extract stream (about 90 per cent furfural) is heated in a furnace and flashed twice—first at high pressure and then at low—to drive off furfural vapors, and final traces are stripped from the extract by steam. The raffinate stream contains about 10 per cent furfural, which is separated in the same fashion, except that the high-pressure flash step is not required.

Dry furfural from the flashing operations is condensed and recycled to the extraction system. Wet furfural from steam stripping is condensed, and the two liquid phases that result—one, principally furfural, the other, principally water—are charged to a settling drum. The furfural layer that separates is stripped of water by countercurrent contact in a tower with dry furfural vapors. Wet furfural taken overhead is condensed and returned to the settling drum.* The water layer from the drum is stripped of its furfural content by countercurrent contact with steam. The wet furfural taken overhead from this tower is also condensed and returned to the settling drum.* Thus, the furfural-water condensates are separated into dry furfural and furfural-free water. Dry furfural is recycled to extraction; the water is discarded.

Modern furfural extraction columns contain about 40 to 50 ft of Raschig rings, with redistribution equipment at about 5-ft intervals (27). Charge rates range from 5 to 25 cu ft of oil per hr per sq ft of column cross section. The temperature of the entering hydrocarbon ranges from 110 to 220°F, the temperature of the entering solvent from 200 to 290°F (11,25). Typical temperatures at the top of the extractor range between 230 and 290°F; bottom temperatures are 30 to 80°F lower (27). Two to five volumes of oil are circulated per volume of oil charged. Furfural loss has been reported to be about 0.03 per cent of the amount circulated (11).

Phenol Extraction.† The solvency properties of phenol are similar to those of furfural, but phenol is toxic and it solidifies at atmospheric temperature. On both counts, special precautions must be used in the design of a phenol unit. On the other hand, phenol is less water-sensitive than furfural. Consequently, the recovery equipment is less complex and somewhat cheaper to operate.

A schematic flow diagram for a phenol-extraction plant is shown in Fig. 11-8. The feed stock is first contacted with waste vapors (principally water vapor) to recover phenol. The feed is then charged to the lower part of a refluxed extraction column, through which it rises countercurrent to the solvent phenol. Reflux is induced by the introduction of

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* Furfural and water form a minimum-boiling-point azeotrope.

† Phenol extraction was developed by the Standard Oil Co. (Indiana), Standard Oil Co. (New Jersey), Union Oil Co., and M. W. Kellogg Co.

water at the bottom of the column. (The solubility of hydrocarbons in phenol is reduced by the addition of water.) The rich extract is fractionated to drive off its water content, the water-phenol vapors taken overhead being sent to the phenol absorber. Both the extract and the raffinate phases are then heated and flashed to separate the bulk of the phenol, which is recycled to extraction. Residual phenol is then stripped from both streams by steam in vacuum towers. A part of the overhead vapors (principally steam) is condensed and returned to the bottom of the extractor to induce reflux. The rest is discarded after giving up its phenol content to the feed in the initial absorption column.

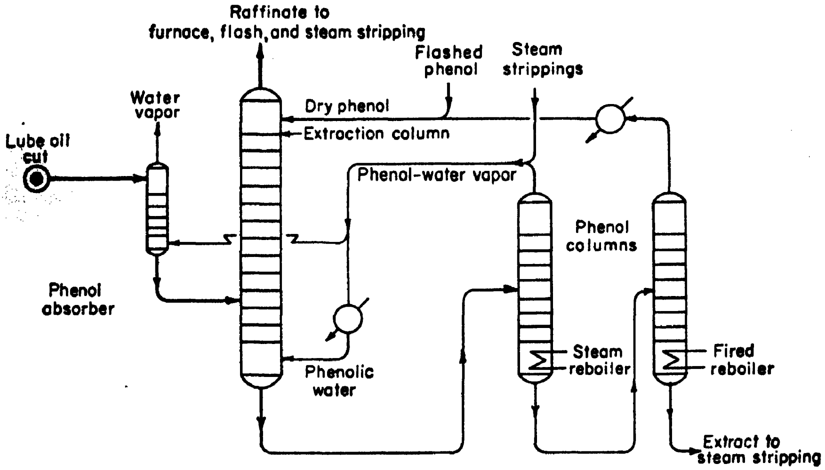

FIG. 11-8. Phenol extraction.

With certain feed stocks, aqueous phenol must be used to permit adequate separations of the phases. With a California low-cold-test oil, up to 12 per cent water is used (11).

Most phenol extraction columns contain 14 to 20 perforated trays, and oil charge rates range from about 5 to about 15 cu ft per hr per sq ft of column cross section (27). The phenol system operates at slightly lower extraction temperatures than the furfural system. Column-top temperatures range between 155 and 255°F; bottom temperatures are 10 to 75°F lower. The amount of solvent circulated ranges from 1.4 to 8 times the oil charged. Phenol losses have been reported at 0.02 to 0.03 per cent of the amount circulated (11,37).

Duo-Sol Extraction.* The Duo-Sol process employs two solvents which are substantially immiscible—propane and a phenol-cresol mixture called Selecto. Propane dissolves noncyclic materials preferentially

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* Duo-Sol extraction was developed by the Max B. Miller Co.

and precipitates asphalt. Selecto preferentially dissolves asphalt, polycyclic aromatics, and color bodies. Thus, the Duo-Sol process has a dual function: it removes asphalt as well as the undesirable hydrocarbons removed in the other extraction processes. Because it employs two solvents, however, the equipment required for the Duo-Sol process is more complex.

A schematic flow diagram for a Duo-Sol unit is shown in Fig. 11-9. The extraction equipment consists of seven to nine mixer-settler stages which operate in series. Propane is charged to one end stage, a mixture of phenol and cresol to the other. The two solvents pass through the extractors countercurrently. Feed is charged to an intermediate stage, where it distributes itself between the two solvents. The raffinate-rich propane stream passes countercurrent to the entering phenol-cresol stream, which purifies the raffinate by extracting residual asphalt and polycyclics. The extract-rich phenol-cresol stream passes countercurrent to the entering propane stream, which strips raffinate-type materials from the extract and thus improves recovery. The raffinate and extract are stripped of their propane and phenol-cresol contents by several stages of evaporation and steam stripping.

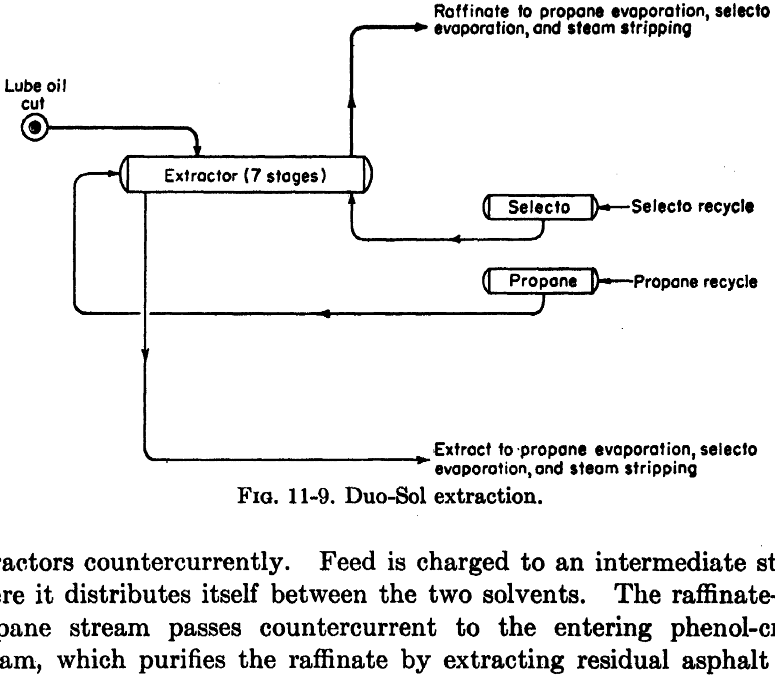

FIG. 11-9. Duo-Sol extraction.

Mixer-settlers are usually used in the Duo-Sol process (27), which operates at temperatures from 60 to 150°F (11). The upper temperature is limited by the vapor pressure of propane, the lower temperature by crystallization of wax or phenol. The amounts of propane and phenol-cresol circulated are usually about four times the oil processed. Propane losses are reported at about 0.2 per cent of the circulation; phenol-cresol at about 0.03 per cent (11). The water content of the phenol-cresol mixture is held below 0.15 per cent (32).

LUBRICATING-OIL-FINISHING OPERATIONS

Lubricating-oil stocks require finishing operations to meet specifications such as color and emulsibility. With solvent-extracted stocks a clay treatment is usually sufficient. With unextracted stocks, acid treating and clay treating may be required. About 1955, hydrogen treating was proposed as an alternate to these treating procedures. All the treating operations are covered in Chap. 13.

TYPICAL LUBRICATING-OIL PLANTS

Lubricating oils are used in a wide variety of applications, ranging from transformer oils with viscosities of 60 SSU at 100°F to heavy cylinder oils with viscosities of 200 SSU at 210°F. In view of this wide variation in oil requirements, the manufacturer does not attempt to produce each oil directly. Rather, he produces a number of base stocks, which are blended together in varying proportions to make the desired products.

Whatever its application, a lubricating oil must be stable, have a high flash point, and retain its lubricating properties in service. Further, it must not contain so much wax that it congeals at operating temperatures, and its viscosity must be suitable for the load and temperature conditions under which it is to be used. In view of these circumstances, base stocks for blending are generally segregated on the basis of pour point, viscosity, and viscosity index.

Separation of the original reduced crudes into base stocks of different viscosities is usually carried out in the first manufacturing step, vacuum distillation, and the several distillates are then kept separate through the entire manufacturing procedure up to the final blending step. As a consequence, the capacity of each processing unit varies, depending upon which particular stock is being treated. Although modern dewaxing plants could operate on stocks containing both paraffin and microcrystalline waxes, the base stocks are usually fractionated to segregate the paraffin wax; this move simplifies the subsequent wax operations.

The facilities which are used in any given plant depend on a large number of factors. Two of the principal ones, of course, are the qualities of the available crudes and the characteristics of the products to be made. A third factor of considerable importance is how the plant developed. A less economic process will be retained after a better one is developed if the improved process does not have sufficient advantage to warrant retiring the existing plant. For example, solvent extraction may have sufficient advantage to retire acid treating for the manufacture of high-viscosity-index oils, but not for the manufacture of low-viscosity-index oils. How the type of crude available may affect the type of equipment used is illustrated in Figs. 11-10 and 11-11.

The plant shown in Fig. 11-10 has some desirable mixed-base crude available, but not sufficient for the entire lubricating-oil budget. Consequently, it is necessary to employ a less-desirable naphthenic crude also. Satisfactory high-viscosity-index oils are made from the mixed-base crude by vacuum distillation, extraction, dewaxing, and claying. The same sequence of operations is required to produce satisfactory low and medium VI oils from the naphthenic crude. Thus, all the oils produced in this plant are solvent-extracted. Also, the crudes are carefully segregated because high-viscosity-index oils cannot be made from the naphthenic crude.

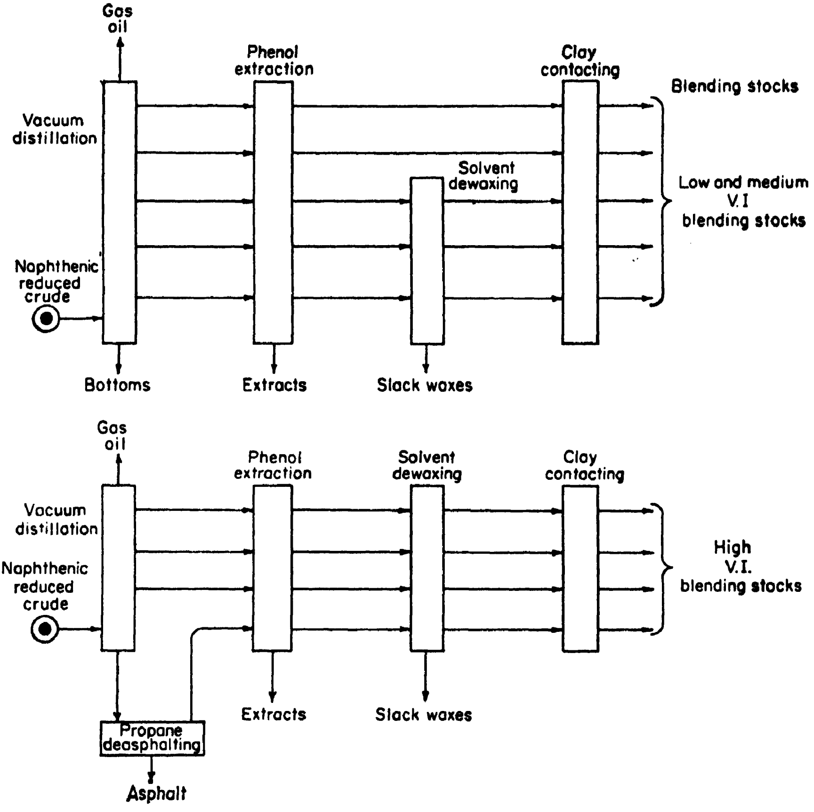

FIG. 11-10. Representative lubricating-oil plant—I.

The plant shown in Fig. 11-11 has sufficient mixed-base crude for the production of the whole lubricating-oil budget. As in the first plant, the high-viscosity-index oils are made by vacuum distillation, extraction, dewaxing, and clay treating. However, oils of low viscosity index can be made without solvent extraction. Consequently, older equipment involving acid treating is still being used for the manufacture of these oils.

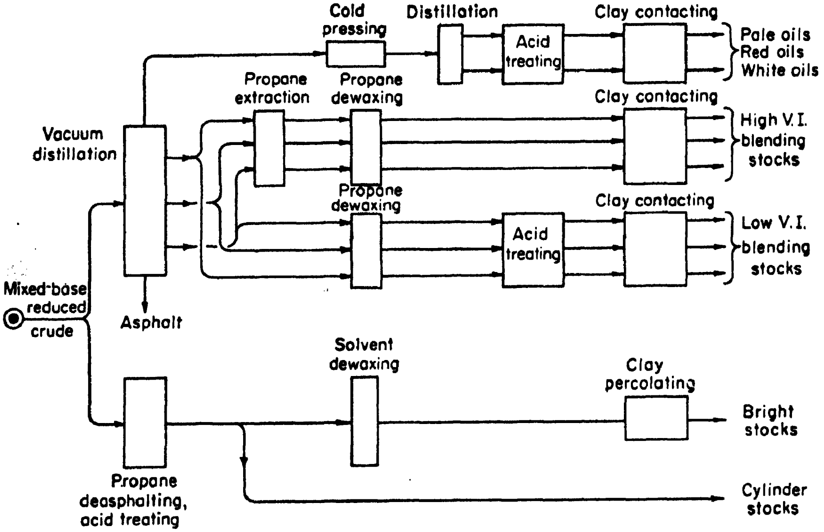

FIG. 11-11. Representative lubricating-oil plant—II.

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CHAPTER 12

HYDROGENATION

It has long been known that petroleum stocks and other carbonaceous materials can be upgraded by hydrogenation. The pioneer experimental work was undertaken by Bergius about 1910 (6), and intensive work by him and others in Germany led to commercial applications* in the late 1920s (20). Because hydrogenation can be used to extend the supplies of petroleum, the process appeared quite promising in the early 1930s—one of the several periods when it was feared that supplies of petroleum were running out—and a few plants were built in the United States, in England, and in Italy to convert lower-boiling stocks into gasoline (9,11,50). When new oil fields were discovered, however, and the threat of a petroleum shortage evaporated, the plants proved to be uneconomical, presumably because of the high cost (16) of manufactured hydrogen.† Nevertheless, hydrogenation was developed on a large scale in Germany prior to World War II, with coal as the principal raw material. The German development was subsidized by the government, which sought to make Germany self-sufficient in liquid fuels (50). Since World War II, German plants have been operated on indigenous and imported petroleum stocks (36,43).

During World War II, hydrogenation was employed to convert petroleum stocks into blending stocks for aviation gasoline by three different routes. Light gas oils were "hydrocracked" to gasoline, *i*-octene was converted to *i*-octane, and the olefins in catalytic-gasoline fractions were saturated (8,11,45,58). *i*-Octene and catalytic gasolines were hydrogenated to meet an aviation-gasoline gum-forming specification that is much more stringent than for motor gasoline; hydrogenation also improves the octane rating of isooctene substantially. Although

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* The early hydrogenation processes were developed by I. G. Farbenindustrie in collaboration with Standard Oil Co. (New Jersey), Royal Dutch Shell, and Imperial Chemical Industries, Ltd. Subsequently, a large number of hydrogenation processes were developed by other companies (40).

† However, one refinery, which went on stream in 1957, supplements its hydrogen production with manufactured hydrogen (14).

all these operations were practical during the war, when the need for aviation gasoline strained the capacity of the industry to produce it, none of them is economic in a peacetime economy, especially since better processes have been developed for producing aviation gasolines.

Other commercial operations that were carried out to a limited extent before World War II were the upgrading of lubricating oils and of heating oils (33). An exhaustive bibliography of hydrogenation work up to 1950 has been published by the U.S. Bureau of Mines (59).

With the development of catalytic reforming and its rapid expansion since 1950, large supplies of hydrogen became available to refiners at fuel value. Consequently, the economics of hydrogenation improved greatly, and units were built rapidly for a wide variety of applications. By 1957, installed capacity was equal to 8 per cent of the refining capacity of the United States, and one refinery had installed hydrogenation capacity equal to 65 per cent of its crude-running capacity (37).

Applications of Hydrogenation

The term hydrogenation covers a wide variety of processes. For convenience, they may be grouped into three broad classifications: hydrogen treating, aromatic saturation, and hydrocracking. These are only rough classifications, which overlap considerably.

Hydrogen Treating. Hydrogen treatments are mild operations that stabilize petroleum products or eliminate "foreign" elements from them. Stabilization results from converting reactive materials, especially diolefins, to less reactive ones. "Foreign" elements removed by hydrogenation include sulfur, nitrogen, oxygen, halides, and trace metals. As discussed in Chap. 13, hydrogen treating is applied to stocks of all boiling ranges, from light naphthas to lubricating oils. Hydrogen treating of fresh feeds to catalytic cracking reduces coke production in cracking by 25 to 30 per cent, increases gasoline yields slightly, and may improve the leaded octane rating of the catalytically cracked gasoline (15).

Saturation of Aromatics. Aromatic saturation may be employed to upgrade distillate fuels or lubricating oils or to improve charge stocks to catalytic cracking, especially recycle stocks.

Large improvements in distillate fuels have been demonstrated experimentally (50,57):

	Feed	Product	Feed	Product	Feed	Product
Aromatic rings, wt %	28	7	20	3	20	2
Cetane number	32	43	46	59	53	69

However, severe conditions are required, and only limited commercial operations of this type have been reported (33). As discussed in Chap. 13, small improvements in cetane number are also obtained under the milder conditions of hydrogen treating.

Hydrogenation of the aromatics in a lubricating oil raises its viscosity index and lowers its viscosity (Table 12-1) (9,18). Both the lower viscosity and the loss in yield of lubricating oil result from cracking reactions that occur under the conditions used to saturate aromatics. Hydrogenated lubricating oils are superior to the best natural products (21), but they proved to be not competitive with solvent-refined oils (33), which were commercialized only a short time after "hydrolubes" were marketed.

Table 12-1

	Feed	Product	Feed	Product	Feed	Product
Lubricating-oil properties:						
Viscosity index	72	101	73	105	68	92
Viscosity, SSU at 100°F	3,100	580	293	174	1,225	565
Yield, vol %:						
Total liquid	100	105	100	104	100	105
Lubricating oil (dewaxed)	.....	68	...	75	.....	75

Although cycle stocks make poor feeds to catalytic cracking, hydrogenation of their aromatics converts them to superior feeds (7,43). The operation is expensive, and less severe treatments, with only partial saturation (7), would probably be more economical. Effects of feed hydrogenation on catalytic cracking are discussed in Chap. 7.

Hydrocracking. Hydrocracking is cracking under a substantial pressure of hydrogen. The hydrogen has two principal functions: to suppress the formation of tar and coke, and under certain conditions, to convert polycyclic aromatics, which are very refractory, to materials which crack more readily. Hydrogen suppresses the production of tar and coke by reacting with the primary products of cracking and thus preventing their condensation into higher-molecular-weight materials (6). By preventing the degradation of feed, cracking in the presence of hydrogen increases the yield of gasoline obtainable. Condensed-ring aromatics in the feed are hydrogenated if the equilibrium relationships are favorable (26), and their hydrogenation further increases the potential production of gasoline.

Any heavy petroleum stock can be hydrocracked, and the cracking can be carried as far as desired. High conversions to gasoline or premium diesel fuel are possible (43). At the present time, the operation most promising economically appears to be mild hydrocracking of petroleum residuums to yield "clean" stocks for further refining.

Reactions

When hydrogen is contacted with a petroleum stock, a wide variety of reactions may occur, depending upon the nature of the feed stock, the catalyst used, and the conditions of reaction. Possible reactions include the conversion of diolefins to olefins, the saturation of olefins, desulfurization, denitrogenation, deoxygenation, dehalogenation, the saturation of aromatic rings, and the cracking of various hydrocarbons. Under some conditions, dehydrogenation reactions may also occur.

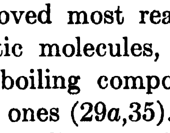
Hydrogen-treating Reactions. Hydrogenation reactions that go easily in the presence of catalysts include the saturation of diolefins and olefins and the removal of "foreign" elements such as sulfur, nitrogen, oxygen, and halogens. Typical examples are

$$CH_2{=}CH{-}CH{=}CH{-}CH_3 + H_2 \rightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$$

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3 + H_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

$$CH_3SH + H_2 \rightarrow CH_4 + H_2S$$

$$CH_3SCH_3 + 2H_2 \rightarrow 2CH_4 + H_2S$$



$$+ 4H_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + H_2S$$

Ease of desulfurization depends upon the type of compound. Sulfur is removed most readily from paraffinic molecules, least readily from aromatic molecules, and naphthenic molecules are intermediate (17). Lower-boiling compounds are desulfurized more readily than higher-boiling ones (29*a*,35).

Some indication of the relative ease of carrying out hydrogen-treating reactions may be seen from Fig. 12-1, which compares the equilibrium relationships for saturating hexene with the relationships for saturating benzene. At the same temperature, a given degree of saturation is obtainable at a much lower hydrogen pressure with hexene than with benzene—and the hydrogenation of diolefins and the removal of foreign elements are usually easier than either.*

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* This difference in equilibrium relationships is utilized in the Autofining process, which was perfected by the British Petroleum Co. (25,41,44,51) just before catalytic reforming made hydrogen available in large quantities. Autofining is a hydrogenation process that generates its hydrogen by dehydrogenating naphthenes in the feed stock; the hydrogen reacts primarily to displace sulfur. In view of the widespread availability of hydrogen, Autofining is of little interest currently.

Saturation of Aromatics. Although all aromatics may be hydrogenated, principal interest is in the conversion of polycyclic aromatics, which are too high-boiling to be included in gasoline and are too refractory to be good charge stocks to catalytic cracking. Monocyclic aromatics, on the contrary, are valuable; lower-boiling monocyclics are high-octane gasoline components, and higher-boiling ones are excellent charge materials for catalytic cracking. Despite this situation, some consideration of the hydrogenation of monocyclics is desirable inasmuch as it sheds some light on the reactions of polycyclics, about which less information is available. Also, monocyclics may be hydrogenated in operations aimed at saturating polycyclics.

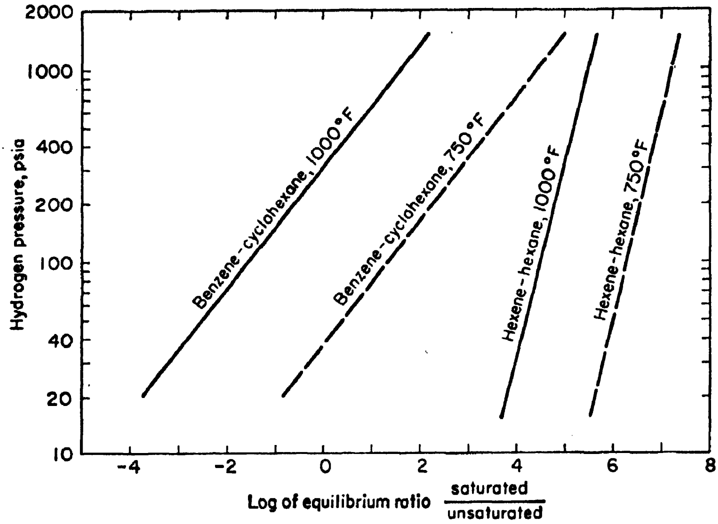
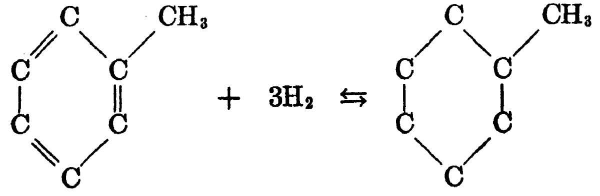


FIG. 12-1. Equilibrium relationships for straight-chain and ring compounds.

Hydrogenation is a reversible reaction, the direction of the reaction depending upon reaction conditions. Equilibrium relationships for the toluene-methylcyclohexane reaction



are shown in Fig. 12-2. For a given degree of hydrogenation, the equilibrium hydrogen pressure rises sharply as the temperature is raised. To achieve satisfactory reaction rates, moderate to high temperatures are required with commercial catalysts; consequently, high hydrogen pressures are necessary for hydrogenation reactions.

The equilibrium relationships of polycyclic aromatics have not been established precisely. Each such system is more complicated than a monocyclic system because there are one or more intermediate products. In the simplest case:

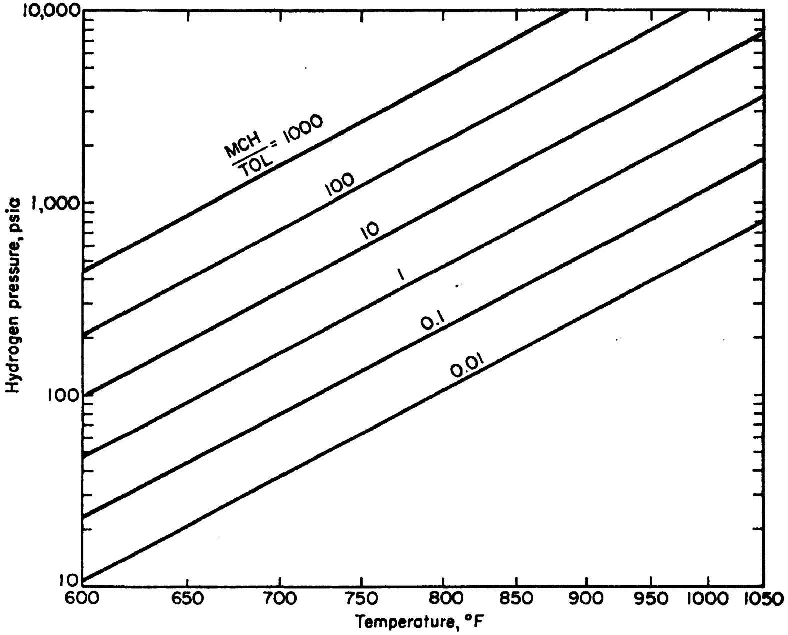
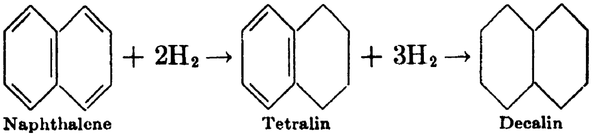


FIG. 12-2. Equilibrium relationships for toluene-methylcyclohexane.



Because more products are possible than with monocyclics, equilibrium relationships are more complex. Experimental data summarized by Sachanen (48,49,50) suggest the approximate equilibriums shown in Fig. 12-3. The relationships appear to be generally similar to those for monocyclics, except that there is a band of conditions, within which considerable amounts of mixed aromatic naphthene molecules, such as tetralin, exist and may predominate. In operations within the shaded area, hydrogenation of aromatics and dehydrogenation of naphthenes may occur simultaneously, the products in both cases being mixed aromatic naphthenes such as tetralin.

When mixtures of aromatics are hydrogenated, the results cannot be predicted from equilibriums alone; the relative rates of reaction must also be taken into account. Relative rates with a nickel-on-alumina catalyst are illustrated in Fig. 12-4. With this catalyst, the first ring of a condensed-ring aromatic is hydrogenated two to five times as fast as benzene or diphenyl, and the final ring is hydrogenated much more slowly (49). The addition of an alkyl group to an aromatic ring slows the hydrogenation reaction. The effect increases with the degree of substitution, and benzene reacts 500 times as fast as hexamethylbenzene (49). Other catalysts give somewhat different results, although qualitative effects of structure on rate are similar (51*a*).

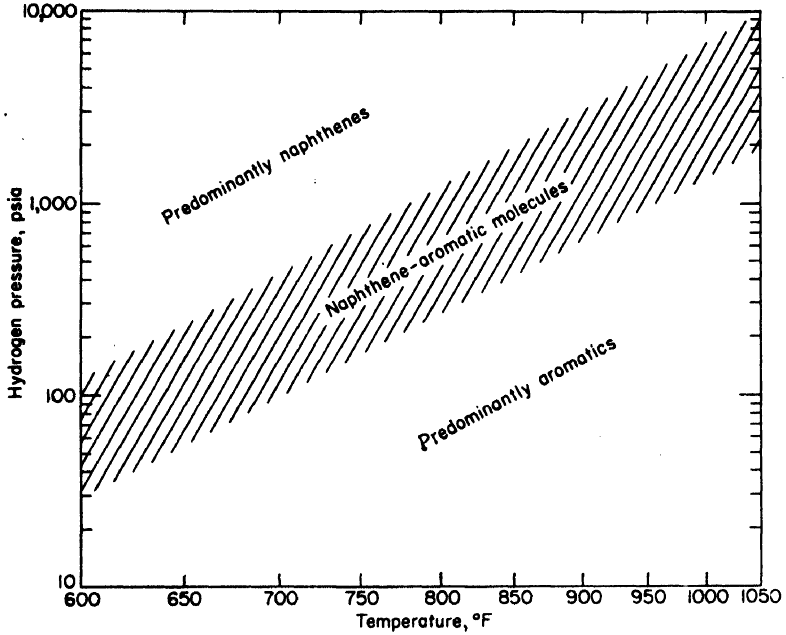


FIG. 12-3. Approximate equilibrium relationships for condensed-ring compounds.

Hydrocracking. Hydrocracking is hydrogenation at temperatures high enough that cracking occurs. The course of the reaction depends upon the nature of the feed and on the relative rates of the hydrogenation and cracking reactions.

With paraffinic feeds, the principal function of hydrogen is to saturate the primary olefinic products of cracking and thus to prevent their condensation to refractory polycyclic molecules. Because paraffins crack less readily than olefins, hydrogenation retards cracking; at high conversions, this effect is more than counterbalanced by the fact that reactants are not degraded to tar and coke and thus they continue to be

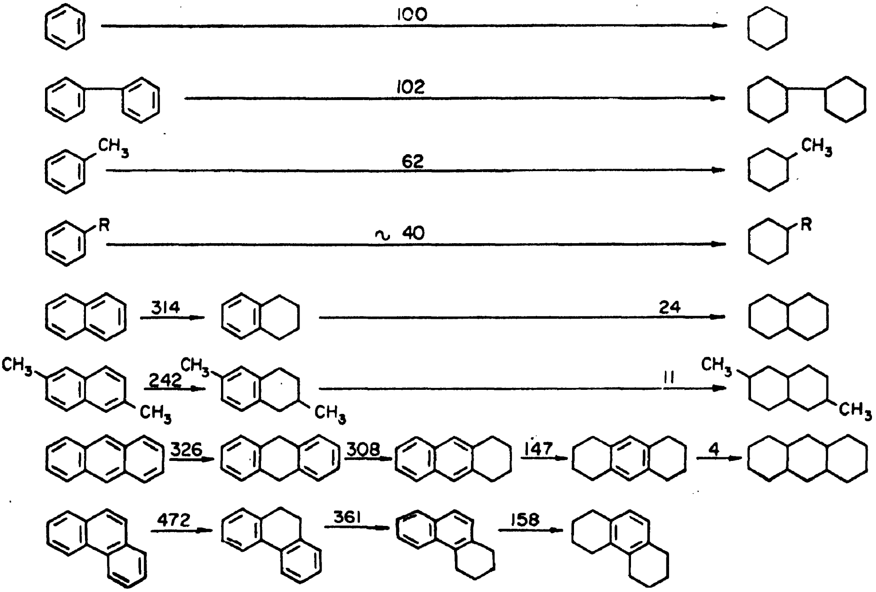


FIG. 12-4. Relative hydrogenation rates.

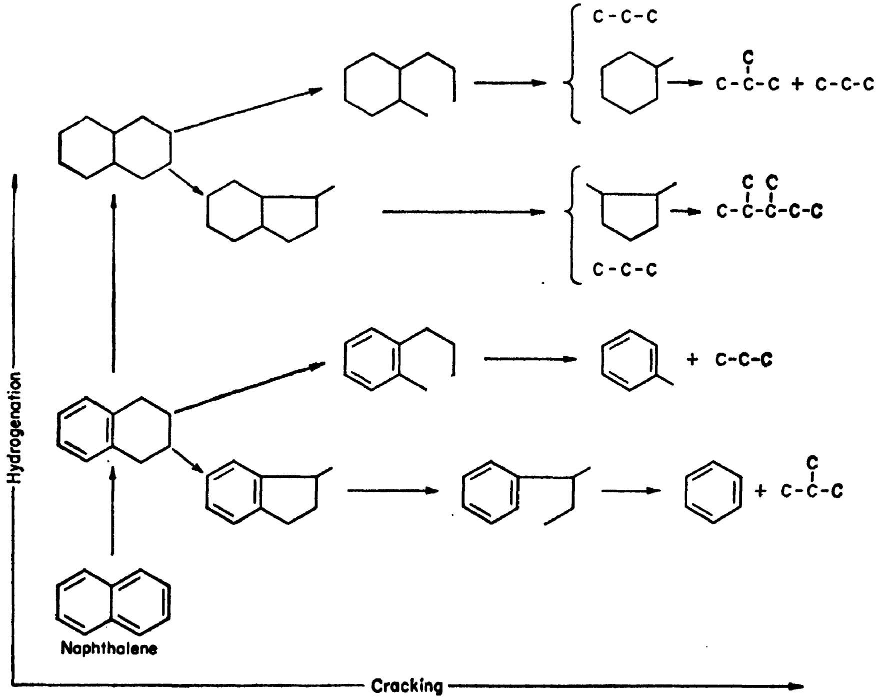


FIG. 12-5. Hydrocracking of naphthalene.

susceptible to cracking reactions. Inasmuch as olefins are hydrogenated under relatively low pressures, increasing the pressure of hydrogen (above some moderate level) probably has little effect on the hydrocracking of paraffins.

In the hydrocracking of aromatics, the course of the reaction depends on the relative rates of hydrogenation and of cracking. Naphthalene, for example, may react as shown in Fig. 12-5 (11). If cracking rates are high relative to hydrogenation, the lower reactions occur, and the product is rich in aromatics. If cracking rates are low relative to hydrogenation, the upper reactions predominate, and the product is *i*-paraffinic.

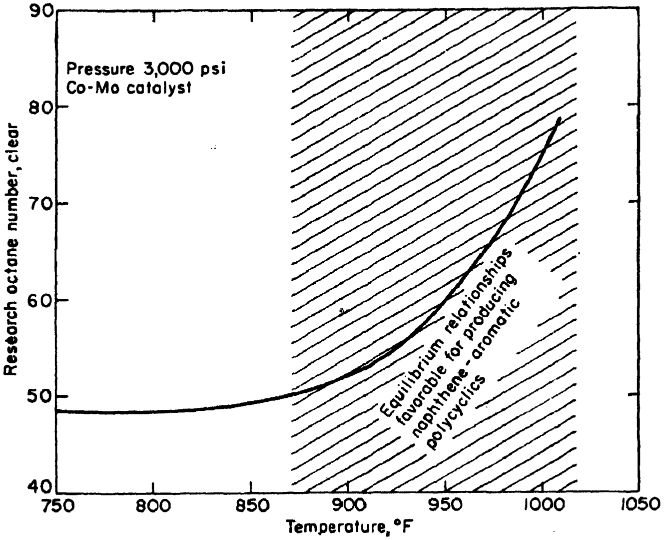


FIG. 12-6. Product octane ratings in the hydrocracking of shale oil (13).

In the hydrocracking of naphthenes, the product is *i*-paraffinic unless conditions are used under which some dehydrogenation is possible. In such cases, decalin, for example, is partially converted into tetralin; and the lower cracking reactions of Fig. 12-5 occur.

How equilibrium considerations affect the course of hydrocracking reactions is illustrated in Fig. 12-6, which shows product octane ratings as a function of temperature in the hydrocracking of shale oil. At low temperatures, which favor the complete hydrogenation of aromatics, the gasoline products had low octane ratings. Increasing the temperature had little effect below temperatures which favor the conversion of condensed-ring molecules to naphthene-aromatic structures. Because materials such as tetralin crack to monocyclic aromatics, further increases in temperature raised the octane rating of the product (13). More gas was produced at higher temperatures and the yield of gasoline was reduced.

Reaction Conditions

Variables of importance in hydrogenation are temperature, pressure, hydrogen charge rate, and oil charge rate.

Temperature. The rates of all reactions increase with temperature, but rates of cracking increase faster than do the rates of hydrogenation or dehydrogenation. Below about 750°F, cracking is usually negligible, and operations in which cracking is not desired are carried out below 800°F. With most hydrogenation catalysts, the rates of cracking double for every 15 to 20°F in the temperature range of 720 to 900°F—approximately the same temperature effect as in thermal cracking (50). Temperatures employed for "destructive hydrogenation" (i.e., with cracking) range between 750 and 1040°F (50).*

Temperature has a much smaller effect on hydrogenation reactions. To double the rate of hydrodesulfurization at about 750°F, for example, required (35) a temperature increase of almost 40°F,† and on the basis of extrapolated data (23), temperature has about the same effect in the hydrogenation of olefins and diolefins. Denitrogenation responds more slowly to temperature (60), and, in the range of 750°F, a temperature increase of 50 to 60°F is needed to double the rate.

Pressure. Pressures employed for hydrogenation of petroleum stocks have ranged from about 200 to 10,000 psi. The pressure employed depends upon the purpose of the operation and the nature of the feed stock.

Hydrogen treating is carried out at pressures of 200 to 1,000 psi, the pressure depending largely on the boiling range of the feed stock and the pressure at which hydrogen is available. Higher-boiling stocks have a greater tendency to deposit coke on the catalyst (4); consequently higher pressures are required for heavier stocks to hold coke deposition at an acceptable level (4,12,28,35). Higher pressures are also required for cracked stocks than for virgin (4). Pressure has little effect on rates of olefin saturation (23); however, increasing pressures increase the extent of reaction by increasing the time of contact between feed and catalyst. The same relationship applies for denitrogenation (60). Desulfurization, on the other hand, increases more slowly with pressure than does olefin saturation (3,10). Therefore, increasing hydrogen

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* However, with some catalysts, appreciable cracking occurs at temperatures as low as 650°F (50).

† Another study (60) indicated a much lower effect of temperature, and the authors concluded that the reaction was diffusion-controlled. However, all the data were obtained at high conversions, which may have been close to equilibrium.

pressures apparently reduce hydrodesulfurization reaction rates, although the increased contact times at higher pressures overbalance the reduction in rates, and the extent of hydrodesulfurization increases as pressure is raised (4,35).

Aromatic saturation can be carried out at low pressures (and low temperatures) in the laboratory. However, catalysts active enough for such an operation are sulfur-sensitive and are not used commercially (47,50,51*a*). With commercial catalysts, elevated temperatures are required, and as shown in Fig. 12-3, high pressures are necessary at moderate to high temperatures. Commercial operations have been at 3,000 psi (7,33).

Hydrocracking can be carried out at any pressure, the principal requirement being a temperature high enough for cracking to occur. If long on-stream periods are intended, the pressure must be high enough to suppress coking, the rate of which increases with temperature (4). Also, if hydrogenation of polycyclic aromatics is desired, the pressure must be high enough for the equilibriums to be favorable. In early operations for the conversion of gas oils to gasoline, pressures were between 3,000 and 10,000 psi (8,11,43). With heavy stocks containing asphaltic materials, coking of the catalyst is substantial even at these high pressures, and in commercial operations, an asphaltic feed is usually pretreated in a liquid-phase operation with an expendable powdered catalyst that is slurried into the feed and separated from the product (43). In experimental work with crude-oil residuums at 3,000 psi, coking of the catalyst has been controlled by careful control of temperatures (42) and by diluting the feed with light hydrocarbons (53). Mild hydrocracking at pressures of 500 to 1,000 psi has also been demonstrated on small-scale equipment, designed for frequent regeneration of the catalyst (19,29). Because the metals present in heavy petroleum stocks are themselves catalysts for hydrogenation, they should not harm most hydrogenation catalysts. In one case 11 per cent of vanadium was shown not to be detrimental (29).

Hydrogen Recycle. In order to ensure a satisfactory hydrogen pressure at the outlet end of a catalyst bed, a substantial excess of hydrogen must be charged with the feed, and the excess is usually recycled. Increasing the hydrogen charge rate slows the formation of coke on the catalyst (19,28). It also increases the rates of hydrogenation reactions (4,19). However, the increased reaction rate is at least partially offset by reduced contact time between feed and catalyst, and the degree of hydrogenation is maximized and then falls off as the hydrogen charge rate is increased (4).

Reaction products, such as hydrogen sulfide, ammonia, water, and light hydrocarbons build up to an equilibrium in the hydrogen recycle gas. Desulfurization is lowered somewhat as the hydrogen sulfide content of the recycle gas is increased (4,19), but ammonia probably has little effect. Light hydrocarbons lower the hydrogen partial pressure; their effects can be counteracted by raising the pressure (19), but the partial pressure of hydrogen must be raised when the hydrogen is fairly dilute (35). Carbon monoxide is a catalyst poison (42).

With stocks boiling below 500°F, enough hydrogen is usually circulated to ensure complete vaporization of the charge stock. With higher-boiling feeds, only part of the feed is vaporized—sometimes a very small part.

Catalysts

A large number of catalysts have been developed for hydrogenating petroleum stocks (11,43). For hydrogen-treating operations, which account for the bulk of the applications of hydrogenation, various cobalt-molybdena catalysts, supported on alumina, dominate the field (11,38). Platinum (52), molybdena (5), nickel-tungsten sulfide, and nickel catalysts have also been used to some extent. Nickel-tungsten sulfide is claimed to have octane advantages for desulfurizing cracked naphthas (1); the saturation of olefins is partly compensated for by isomerization of the remaining olefins (30). Nickel sulfide is used for the selective hydrogenation of diolefins (38).

Hydrocracking catalysts must have their hydrogenation and cracking activities balanced for the particular applications for which they are intended. In the hydrocracking of polycyclic aromatics to gasoline, cracking can proceed only after at least one ring has been saturated, and it is desirable that naphthenic rings be cracked almost as fast as they are produced (11). Thus, reaction conditions that favor the aromatic naphthene structures are favorable. The relative rates of hydrogenation and cracking can be modified by changing the amount of hydrogenating agent incorporated in the catalyst (11,29*a*,43). Among the catalysts that have been used commercially are pelleted tungsten sulfide, tungsten sulfide on natural or synthetic silica-alumina supports, iron on HF activated montmorillonite clay, and nickel on silica-alumina (11,43). Cobalt-molybdena on alumina has been used experimentally (13,19).

Hydrogenation Units

Although hydrogenation covers a wide range of operations, the equipment used in most of them is basically the same.* As shown in Fig. 12-7, feed and hydrogen are heated to reaction temperatures (either together, as shown, or separately), passed down through the reactor, and cooled

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* An exception is the pretreatment of crude-oil residuums in which the catalyst is slurried in the feed (43).

to condense a liquid product. The liquid product is separated from uncondensed gas, which is recycled. To control the build-up of hydrogen sulfide in the recycle gas, it may be scrubbed to remove hydrogen sulfide or a part of it may be rejected as "bleed gas." For processing heavy residues at 500 to 1,000 psi, upflow of feed gases has been considered for both fixed and fluidized beds of catalyst, but the use of downflow fixed-bed reactors is believed to be preferable (28).

Catalyst Regeneration. Most units include provisions for periodic, off-stream regeneration. Deposits are burned off the catalyst at temperatures controlled by mixing steam or recycled flue gas with the combustion air. Typically, regeneration gases enter at 700 to 850°F, and maximum temperatures are in the range of 1100 to 1200°F (29,35,54). After regeneration, the catalyst is in the oxide state. Before being put back on stream, it may be reduced with hydrogen, considerable heat being evolved in the reduction (54).

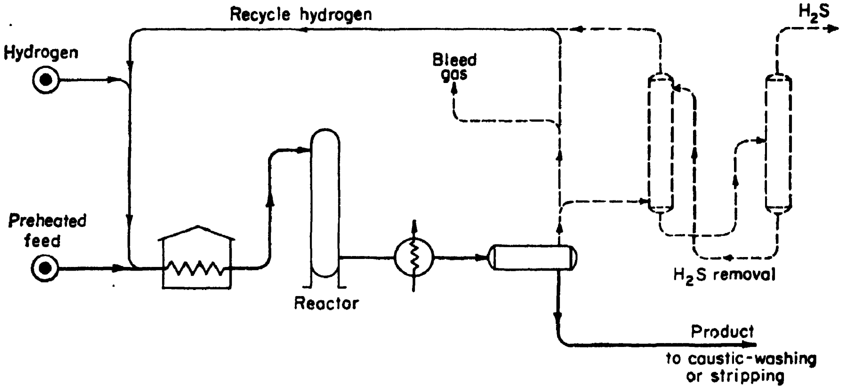

FIG. 12-7. Typical hydrogenation unit.

Temperature Control. Hydrogenation reactions are exothermic (4) and the heat of reaction is roughly proportional to hydrogen consumption.* For operations with high hydrogen consumptions, the catalyst may be divided into a number of beds with cold hydrogen injected between them to control the temperature. As many as ten beds have been used commercially in hydrocracking units (11).

Hydrogen-treating Operations. For hydrogen treating, reported conditions range from 15 to 1,000 psi, 450 to 800°F, 1 to 24 vol of oil per hr per vol of catalyst, and hydrogen-recycle rates of 270 to 6,000 scf per bbl. Operations for which reaction conditions have been reported are listed in Table 12-2.

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* In saturating olefins, about 56,000 Btu are liberated per mole of hydrogen consumed. For desulfurization reactions, the heats of reaction are about half as great (29*a*).

Table 12-2. Hydrogen-treating Operations

Feed	Operation	Catalyst	Press., psi	Temp., °F	H_2 rate		Sp. vel., vol/vol/hr	Reference
					Mole/mole	Scfb		
Butenes or pentenes	Hydrogenation of diolefins	NiS	15–150	480–660	6/1	....	1–2	38
Pentenes	Hydrogenation of olefins	CoMo	50–200	700	.....	1,500	5–10	31
i-Octene	Hydrogenation of olefins	Ni	15–60	360	1.4/1	....	....	56
Cracked naphtha	Hydrogenation of diolefins	W NiS	40–200	400–500	.....	2,000	3–18	23
Virgin naphtha	Desulfurization	Co-Mo	250	700	.....	800	6	38
Virgin-visbreaker naphtha	Desulfurization	Co-Mo	700	700	.....	3,500	5	38
Cracked naphthas	Desulfurization and stabilization	W NiS	500–750	450–700	.....	6,000	5–15	38
Cracked naphthas	Desulfurization	W NiS	720	650	7/1	6,000	10	12
Cracked naphthas	Desulfurization	Co-Mo	300	650–700	3/1	....	3–24	27
Virgin heating oil	Desulfurization	Co-Mo	500	700	.....	2,000	3	38
Catalytic cycle oil	Desulfurization and stabilization	Co-Mo	500	700	.....	3,000	2	38
Catalytic cycle oil	Desulfurization	Co-Mo	750	700	.....	270–1,350	1–2	24
Light gas oils	Desulfurization	Co-Mo	750	710	.....	1,350	1.6	55
Light gas oils	Desulfurization	Mo	500	650–800	.....	>5,000	1–2	38
Light gas oils	Desulfurization	Co-Mo	1,000	780	.....	4,400	4–8	54
Virgin gas oils	Improve feed to cracking	Co-Mo	500	750	.....	2,000–5,000	1.0	15
Visbreaker gas oil	Improve feed to cracking	Co-Mo	500	750	.....	2,000	1.0	15

Hydrocracking Operations. Although hydrocracking has not been economical in the United States, it is practiced on a large scale in Germany (43) and to a limited extent in England (11). In Germany, hydrocracking is favored by the availability of plants built prior to World War II and by the absence of a market for heavy fuel (43). As shown in Fig. 12-8, the original German plants have been augmented with thermal and catalytic cracking facilities that substantially extend their capacities.

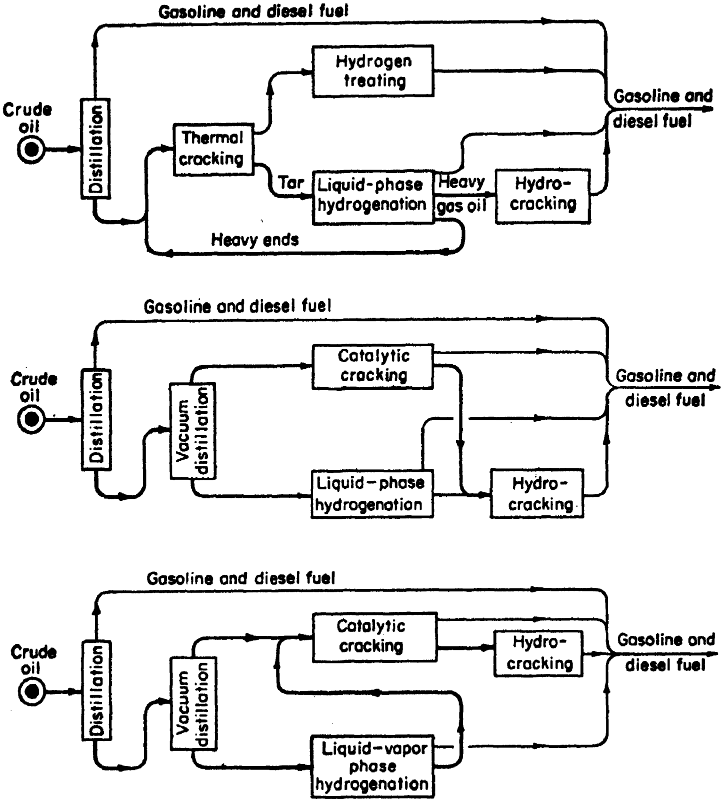

FIG. 12-8. Integrated hydrogenation operations.

Only vacuum-reduced crudes, thermal tars, and catalytic cycle oils are charged to hydrogenation. All of these are poor charge stocks for thermal and for catalytic cracking. From the portions of crude oil heavier than diesel fuels, yields of motor fuels—gasoline and diesel fuels—are 75 to 90 wt per cent of the charge stock, almost as much as obtained by direct hydrogenation. Gasolines from the integrated operations have somewhat higher octane ratings than from direct hydrogenation, and investment and operating costs are lower (43).

In the United States, considerable experimental work has been done

Table 12-3. Hydrocracking Operations

Feed	Crude oil (29)		Reduced crude (29)		Reduced crude (42)		Reduced crude (53)		Asphalt (19)	
Pressure, psi	500–1,000		500–1,000		3,000		3,500		400–800	
Temperature, °F	750–850		750–850		.....		820		725–825	
Diluent	None		None		None		Butane, 50%		Heating oil	
Recycle-gas rate, scf/bbl	2,500–10,000		2,500–10,000		.....		2,300		1,500–4,500	
	Charge	Product	Charge	Product	Charge	Product	Charge	Product	Charge	Product
Yields, vol. %:										
C_4's	2.4[a]	3.1[a]	......	1.3	......	2.5	......	1.1	.....	
Gasoline	25.6	39.0	......	25.7	......	19.8	......	20.3	.....	12.1
No. 2 fuel oil	22.6	34.3	......	41.1	......	24.0	......	66.5	.....	16.4
Gas oil	49.4	19.6	......	27.1	......	29.1	......		.....	31.2
Bottoms			100.0	4.1	100.0	29.4	100.0	18.2	100.0	45.2
Total	100.0	96.0	100.0	99.3	100.0	104.9	100.0	106.1	100.0	104.9
Sulfur, wt %:										
Gasoline	0.09	0.04	......	0.07	......	0.06	......	0.03		
No. 2 fuel oil	1.21	0.47	......	0.16	......	0.17				
Gas oil	4.11	0.84	......	0.42	5.32	0.64	......	0.15		
Bottoms			5.45	3.72		2.52	0.58			
Carbon residue, wt %:										
Gas oil	9.8	0.88	......	0.59	17.2	......	......	3.6		
Bottoms			19.8	32.9		......	5.9			

[a] Includes C_3.

on mild hydrocracking of crudes and reduced crudes (19,29,53), but no commercial operations have been reported. Reported small-scale results are given in Table 12-3.

Preparation of Feeds. To minimize fouling of heat-exchange equipment, the feed stock is sometimes stripped to eliminate oxygen, which promotes the formation of gummy deposits on heat-transfer surfaces (54). Alternatively, freshly distilled feed may be charged, or the feed may be stored in gas-blanketed tanks.

Table 12-4. Investment Costs for Hydrogenation

Charge stock	Charge rate, bbl/day	Investment, $ per bbl/day	References
Naphtha (300–400°F)	5,000	100 (1955)	22
Cracked naphtha	10,000	200 (1955)	1
Naphtha (210–500°F)	5,000	150[a] (1955)	22
Distillate fuel	1,000	250 (1956)	38
Light virgin gas oil	10,000	93 (1953)	55
Heavy virgin gas oil	5,000	140 (1955)	22
Light catalytic cracked gas oil	10,000	130 (1953)	55
West Texas crude	20,000	450[b] (1956)	29
Residuum—light catalytic cycle oil	20,000	770[b] (1956)	29
Residuum	5,000	840 (1957)	42
Residuum	14,000	800[b] (1957)	42

[a] Includes a product fractionator.

[b] Includes hydrogen-manufacturing facilities.

Because hydrocracking catalysts are sensitive to nitrogen-containing compounds, feeds high in nitrogen may be hydrogen treated before they are hydrocracked (11,43). To ensure complete removal of basic nitrogen compounds, a hydrogen-treated feed may also be washed with sulfuric acid (11).

Materials of Construction. In the construction of hydrogenation plants, materials resistant to hydrogen and hydrogen sulfide must be used at temperatures above 500°F (39). In one commercial unit (54), 18-8 stainless steel was used for all surfaces above 500°F to avoid the "formation of sulfide scale that would otherwise carry forward in the combined recycle gas and oil stream and settle as a pad on top of the catalyst bed." Reactor shells can be made of carbon or carbon-molybdenum steels if they are lined with castable refractory and insulating cements (39). A stainless steel or aluminized low-chrome steel liner is often used to prevent bypassing of reactants through cracks in the cement. Generalized correlations of corrosion by hydrogen–hydrogen sulfide mixtures have been published (2,34).

Investment and Operating Costs

Published investment costs for hydrogenation units are listed in Table 12-4. Operating costs depend both on the type of operation and the size of the unit. For hydrogen-treating units with capacities of 5,000 to 10,000 bbl per day, most published costs (1957) range between 7 and 15 cents per bbl. Much higher figures are quoted for mild hydrocracking of a crude oil (25 cents per bbl) and a reduced crude-cycle oil mixture (75 cents per bbl); both of these figures are for 20,000 bbl per day units, and they both include hydrogen-manufacturing costs, which are substantial. For processing reduced crudes, operating costs of 35 cents per bbl are claimed for 5,000 bbl per day units operating with reformer hydrogen and for 14,000 bbl per day units employing manufactured hydrogen (42). Typical utilities requirements are listed in Table 12-5.

Table 12-5. Utilities Requirements for Hydrogenation

	Light catalytic cycle oil			Virgin gas oil	Crude oil
	(38)	(55)	(39)	(55)	(29)
Charge, bbl/day	10,000	10,000	8,500	10,000	10,000
Steam, lb/hr	25,000[a]	......	2,660[a]	9,000	22,000
Power, kw	200	760	245	360	250
Fuel, 1,000,000 Btu/hr	10	10	21	16	19
Water, gpm	3,000	5,000	1,860	1,200	6,800

[a] Steam, 100 to 125 psi.

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CHAPTER 13

ACID, CLAY, AND HYDROGEN TREATING

Virgin and cracked materials frequently require various finishing treatments to make them salable. Usually, any resinous, asphaltic, or unstable compound must be removed, and sulfur compounds and aromatics are also undesirable in many cases. Commercially, such materials are removed by acid treating, clay treating, or mild hydrogenation. Stocks of all boiling ranges are treated.

Cracked gasolines contain unstable materials which form gum or develop color in storage, and some cracked gasolines contain considerable amounts of sulfur compounds also. Before 1924, acid treating was used extensively to remove both types of contaminants. A mild acid treatment (59) removes the unstable gum-forming and color-forming materials, which are principally diolefins (30); a severer treatment removes sulfur as well. In 1924, the first of several clay-treating processes for removing gum formers and color formers from cracked gasolines was commercialized (37); these processes displaced acid treating of cracked gasolines, except where sulfur removal was necessary. Clay treating was in turn made obsolete in the 1930s by the invention of additives to inhibit the gum-forming reactions,* and by the advent of dyeing of gasolines, which made the color of gasoline stocks unimportant. Severe acid treating to reduce the sulfur content of gasoline is still being practiced, but hydrogenation processes may displace it also.

Virgin gasolines have been desulfurized by passage over bauxite catalysts at elevated temperatures. With hydrogen available from catalytic reforming, hydrogenation is competitive for this operation, and an acid-treating process is claimed to be cheaper (54).

Distillate fuels have been acid treated to remove aromatics, to improve the colors and odors of virgin stocks, or to remove unstable materials from cracked stocks. Solvent extraction is now used to separate aromatics, and catalytic hydrogenation processes are taking over the sulfur, odor, and stability problems.

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* The formation of gum is initiated by oxidation of diolefinic materials (21). The additives prevent this oxidation and they are therefore called antioxidants.

Lubricating-oil stocks are processed to remove aromatics and thus improve viscosity indexes and reduce tendencies to oxidize. They are also processed to stabilize and decolorize them by removing asphaltic and resinous materials. In older plants, these objectives are accomplished by treating the stocks first with acid and then with clay. Lubricating stocks are still produced in this way, but newer plants employ extraction and precipitation procedures in place of acid treating. Hydrogenation processes are also alternates to acid treating and clay treating.

Other products which have been finished by acid treating, and/or clay treating include benzene, toluene, high-solvency naphthas, dry-cleaning fluids, refrigerator oils, transformer oils, turbine oils, white oils, and medicinal oils. Most of these will probably continue to be finished by current treating procedures.

Sodium has also been proposed as a treating agent for stabilizing or for desulfurizing petroleum products.

SULFURIC ACID TREATING

Sulfuric acid was used as a petroleum-refining agent as early as 1855 (20,33). As time passed, numerous applications were found; in fact, it seemed that almost any product-quality problem could be solved by acid treating, and the use of sulfuric acid increased very rapidly. By 1936, the petroleum industry was the second largest consumer (10).

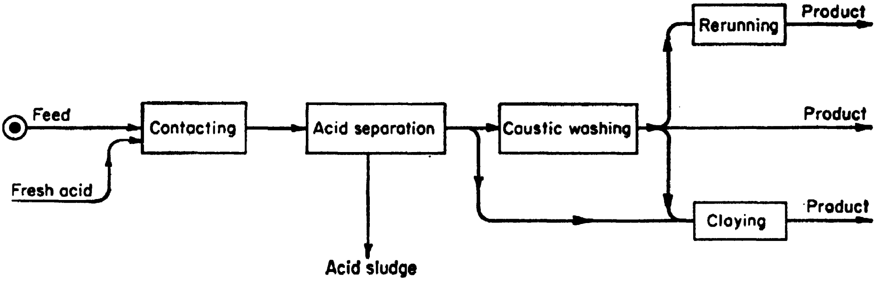

FIG. 13-1. Schematic acid-treating diagram.

In recent years, technological developments have displaced acid treating for particular applications; nevertheless, sulfuric acid is still the most-used refining agent. It is used for finishing petroleum products of all boiling ranges. In all cases, the operations are similar, as shown schematically in Fig. 13-1. Raw stock and acid are brought together in the desired proportions, generally at or near atmospheric temperature. After thorough contacting, the phases are separated, the hydrocarbon phase is neutralized by caustic washing, claying, or both, and the spent-acid phase is discarded. Sometimes, the product is fractionated (rerun) to remove high-boiling material formed in the treating operations.

The mechanism of acid treating is very complex, and it varies with the feed stock, the acid concentration, the temperature, and the reaction time. Sulfuric acid functions in three general ways (20,59):

1. It reacts with certain of the compounds in the charge stock, particularly with olefinic or asphaltic materials, and, under drastic conditions, with aromatics also. The "sludge" which results dissolves in the acid phase.
2. It extracts certain sulfur-containing materials, especially alkyl sulfides and thiophenes.
3. It causes olefins to react either with other olefins or with aromatics. Polymerization is the major reaction, and most of the polymer remains in the hydrocarbon phase.

Desulfurization of Cracked Gasoline

In the desulfurization of cracked gasolines, the degree of desulfurization depends on the amount of acid, the concentration of the acid, and the number of contacting stages used. Because sulfur usually concentrates in the higher-boiling fraction of gasoline, the lighter portion is frequently bypassed around the treating operation (20,59).

Operating Conditions. Desulfurization increases with acid usage. Data for several gasolines (18,59,65) are correlated in Fig. 13-2. For these gasolines at least, sulfur removal per unit of acid appears to be constant down to a residual sulfur level of 0.10 to 0.15 per cent. Further reduction of the sulfur content increases acid requirements sharply.

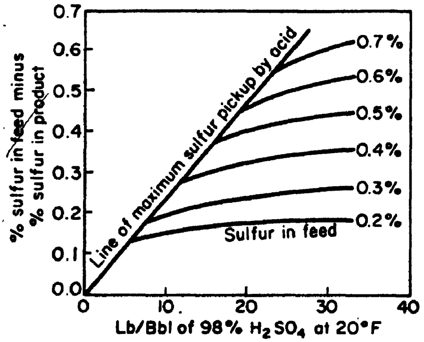

FIG. 13-2. Desulfurization of thermally cracked gasolines in one-stage acid treating.

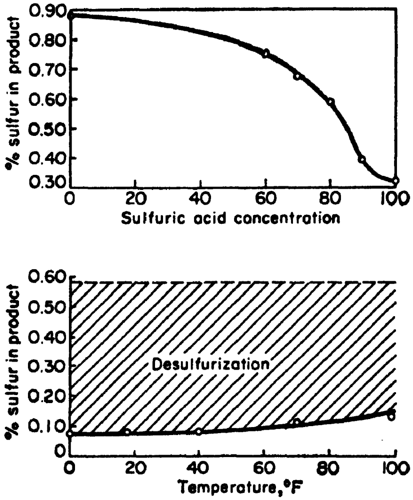

FIG. 13-3. Effects of sulfuric acid concentration and temperature on desulfurization of a cracked gasoline (20,59).

The effect of acid concentration on desulfurization is shown in Fig. 13-3.

Below 60 per cent, the acid is ineffective. Its effectiveness increases rapidly up to about 93 per cent concentration, less rapidly at higher concentrations.

Countercurrent multistage treatment makes the acid more effective. In a commercial three-stage plant (2), the acid was reported to be more than twice as effective as indicated in Fig. 13-2 for single-stage operations.

Product Yield and Quality. Desulfurization of a cracked gasoline with sulfuric acid is accompanied by a gasoline loss. This loss results from two distinct effects: formation of sludge and production of polymer, the polymer being fractionated out of the product. The results in Table 13-1 have been reported for single-stage treating of a cracked California gasoline at room temperature (20). The ratio of gasoline loss to sulfur reduction increases with treating severity over the whole treating range. Although mercaptans are removed by sulfuric acid, complete sweetening is not attempted commercially because the treating losses and the acid requirements would be excessive (34).

Table 13-1

	Acid (93%), lb/bbl					
	0	1.5	5	10	20	30
Sulfur content, %........	0.61	0.55	0.48	0.41	0.25	0.14
Sludge loss, %...........	....	0.3	1.0	2.3	4.4	6.7
Polymer loss, %..........	....	0.5	1.0	1.9	3.2	4.7
Total loss, %..........	....	0.8	2.0	4.2	7.6	11.4

Desulfurization is improved by reducing the treating temperature, as shown in Fig. 13-3, and losses to sludge and to polymer are reduced. The relationship in Table 13-2 has been reported for treating with 98 per cent acid (20). Losses are also affected by contact time, as shown in Fig. 13-4. Equilibrium with regard to sulfur content is reached in about 10 sec, whereas polymerization losses continue to increase with time.

Table 13-2

Sulfur content, %	Acid required, lb/bbl			Treating loss, %		
	20°F	60°F	No control	20°F	60°F	No control
0.37						
0.25	4.0	3.5	5.5	2	3	6
0.20	5.5	5.0	8.5	3	4	8
0.15	8.0	8.0	13.0	4	6	12
0.10	12.0	14.0	27.0	6	10	20

Acid treating usually reduces the octane number of an unleaded gasoline, the loss resulting from the polymerization of olefins and diolefins (18). On the other hand, treated gasolines respond better to the addition of tetraethyllead, primarily because of the removal of sulfur compounds, which tend to counteract the effect of tetraethyllead. Because polymerization is reduced at lower temperatures, octane losses are also less (65).

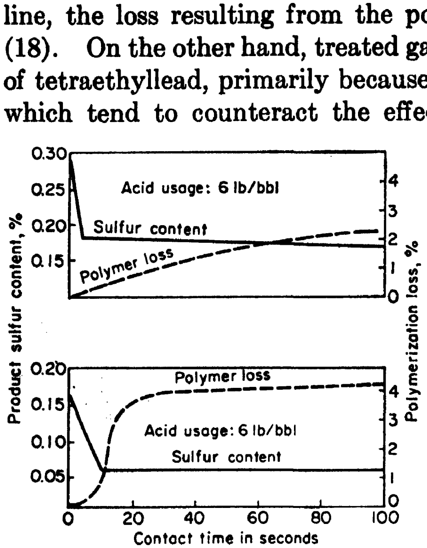

FIG. 13-4. Effect of contact time on acid-treating losses of two cracked gasolines (59).

Rerunning Operations. Acid-treated gasolines are distilled, or rerun, to eliminate the polymer formed in treating. Rerunning must be carried out carefully to avoid decomposition of high-boiling dialkyl esters and disulfides, which are present in the treated stock. In some cases, steam or vacuum distillation is used to hold the temperatures down. In others, sodium carbonate is added to the charge to neutralize any acidic materials formed during the distillation. Maximum temperatures recommended for rerunning are 250 to 300°F (30,46).

Treating of Distillate Fuels

A virgin distillate fuel is acid treated to reduce its sulfur content or to improve its color and odor (62). Most of the odor improvement results from converting mercaptans to disulfides:

$$\begin{aligned} RSH + H_2SO_4 &\rightarrow RS{-}SO_3H + H_2O \\ RSH + RS{-}SO_3H &\rightarrow (RS)_2SO_2 + H_2O \\ (RS)_2SO_2 &\rightarrow R_2S_2 + SO_2 \end{aligned}$$

Typically, use of 6 lb of 98 per cent sulfuric acid per barrel of charge converts about 90 per cent of the original mercaptans to disulfides. Treating temperatures of 90 to 130°F are generally used (40).

A cracked distillate fuel is sometimes acid treated to improve its stability by removal of resinous and gum-forming materials. For example, light catalytic cycle oil may be treated with about 2 lb of 75 per cent acid per barrel of feed before it is blended into No. 2 fuel oil. However, the offending materials are often acidic (70); they then can be removed by a simple caustic wash (7,66).

Treating of Lubricating Oils and Other Stocks

Lubricating oils may be acid treated to remove aromatics and asphalts (23). For the production of lubricating stocks of high viscosity index, the treating requirements depend upon the concentration of aromatics in the original stock, because aromatics have low viscosity indexes; acid requirements may be as high as 75 lb per bbl, and yields of finished oils are low. When oils are treated only to improve color and resistance to oxidation, treating requirements range from about 15 to 25 lb of 93 per cent acid per barrel of charge. Acid-treated stocks are usually clay treated to remove residual contaminants and entrained acid.

Other stocks that may require acid treating include nitration-grade aromatics, solvents, and various specialty products. Typical treating requirements for some of these stocks are listed in Table 13-3. Medicinal oils require the most severe treatment—as much as 300 lb of oleum per barrel of feed.

Table 13-3. Typical Acid Requirements in Treating Various Oils

	Lb/bbl	Per cent acidity
Benzene, nitration grade	5	98
Toluene, nitration grade	7	98
High-solvency naphthas	8	98
Dry-cleaning fluids	20	98.5
Insecticide base oils	90	104.5
Cutting oils	10	93
Refrigerator oils	40	93
Transformer oils	70	98
Turbine oils	85	104.5
Technical white oils	125	104.5
Medicinal oils	300	104.5

Operating Procedures

Acid treating is carried out commercially in continuous and in batch units. Larger-volume light products are usually handled in continuous units. High-boiling and smaller-volume products are often handled batchwise. Both loss of oil and consumption of acid are lower in a continuous unit. Operating costs are also lower, but the differences may not be sufficient on a small-volume product to justify the larger investment required.

Continuous Units. Continuous units have one to three treating stages. A two-stage unit for treating a sour No. 1 fuel oil is shown in Fig. 13-5. Feed is charged to first-stage mixers, where it is contacted with acid from the second stage. The resulting mixture is settled to separate the oil phase from spent acid, which is discarded. Separated oil is contacted with fresh acid in second-stage mixers, and the mixture is again separated by settling, the acid phase being sent to the first-stage mixers. Treated oil is then passed through a packed column to coalesce small droplets of entrained acid into larger particles, which are settled out of the oil and returned to the first-stage mixers. Water washing and caustic washing the product removes any remaining traces of acid. In some installations, electrical precipitation is used instead of settling for separating acid or caustic from the oil phase (47,52,53,66). Separation is accomplished by passing the aqueous emulsion through a high-potential electric field, which causes electrolytes to coalesce into the water phase. Better efficiency in the use of chemicals is claimed in conjunction with electrical precipitation because greater mixing intensities are permissible in the contacting step.

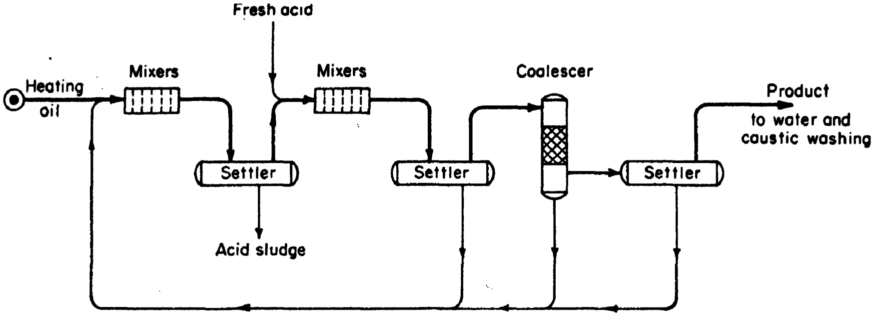

FIG. 13-5. Acid treating of a sour heating oil.

Similar equipment is used for treating cracked gasolines, except that the reactants are cooled between stages, centrifuges are often used for separating the phases in order to minimize contact time, and the product is fractionated to eliminate polymers. Refrigeration may be used to reduce the treating temperature. Three commercial plants for treating cracked gasolines have been described in the literature (2,58,59). All three are three-stage units employing 98 per cent acid and operating at temperatures of 0 to 30°F. In one of the units, 6.5 lb of acid per barrel of charge reduces the sulfur content from 0.6 to 0.25 per cent, with a yield of 94 per cent and a clear octane loss of one unit.

At least two continuous plants have been built to treat lubricating oils (47,49). Both employ electrical precipitation. Operating temperatures range from 100°F for light stocks to 170°F for heavy stocks. Advantages claimed are reductions in oil losses and in acid requirements. Both are said to be reduced about 25 to 50 per cent from the levels experienced in batch operations.

In the treating of benzene, toluene, and high-solvency naphthas, single-stage units are generally employed. As in the case of gasoline, the products are rerun to eliminate polymers.

Batch Units. Batch operations are carried out in large cone-bottomed "agitators," which range up to 4,000 bbl in size (23). Agitation is accomplished—usually for about 30 to 60 min—by blowing the vessel contents with air or by circulating the oil through the acid phase. The reactions are exothermic. Temperature is generally held below 120°F, and this restriction limits the acid charge to about 20 to 30 lb of acid per barrel of oil charge. For severe treating, the process is repeated as many times as is necessary, and the oil is cooled between treatments. The products from batch treating are finished by neutralization, either by aqueous sodium hydroxide, the "wet method," or by clay contacting and filtration, the "dry method." Sometimes both methods are used.

Production of By-products. In the manufacture of certain products, such as "white oils," the intermediate and the final products may be washed with 60 per cent alcohol to remove sulfonic acids. These acids are converted to the corresponding soaps by reaction with caustic. The soaps may be recovered and sold as "mahogany soaps," which are useful as emulsifying agents. White-oil sludges are also processed to recover water-soluble sulfonic acids, or "green acids," which are powerful demulsifying agents.

Production of Acid. Large refiners often produce their own sulfuric acid in conventional contact plants, which burn sulfur to sulfur dioxide, oxidize the sulfur dioxide to trioxide over a vanadium catalyst, and absorb the sulfur trioxide in sulfuric acid. Sulfur is often produced from hydrogen sulfide recovered from refinery gases (15,17,61). One-third of the hydrogen sulfide is burned to sulfur dioxide, which is reacted with the remaining hydrogen sulfide over a bauxite catalyst to produce sulfur and water.

Disposal of Sludge. Sludges produced in acid treating contain from 25 to 70 per cent acid, and they pose major problems of disposal. Dumping them would pollute water streams, and burning them liberates large quantities of sulfur dioxide into the atmosphere. Sludges may be processed to recover acid, but the operations are usually costly. Nevertheless, they are frequently used as the only practical means of disposal. Acid may be recovered either by hydrolysis and reconcentration or by coking (31).

Sludges are hydrolyzed by adding sufficient water to produce a 30 per cent acid; most of the hydrocarbons then separate as a "liver," which is burned as fuel. Hydrolyzed acid is concentrated by direct contact with hot flue gases to evaporate water in two or more countercurrent stages. Reconcentration is limited to an acid strength of 90 to 93 per cent (31).

If higher concentrations are attempted, the acid reacts violently with dissolved oils.

Sludges are coked by heating them to about 450°F. Heat is supplied by a circulating stream of coke, which is heated to 1100 to 1200°F by direct exchange with flue gas in a revolving kiln. Hot coke passes through a star valve into a decomposing chamber, where it contacts the sludge feed, which decomposes into coke, sulfur dioxide, and some hydrocarbon gases. The sulfur dioxide is then converted to sulfuric acid by a modified contact process, in which light hydrocarbons are burned and excess water produced in the burning is removed. Acid recovery averages about 85 per cent.

CLAY TREATING

Clay treating is used to decolorize and stabilize cracked gasolines, to desulfurize virgin gasolines and kerosenes, to decolorize heavy-oil products, to "neutralize" acid-treated heavy oils that cannot be caustic-washed because of emulsification difficulties, and to remove arsenic from charge stocks to reforming. In the treatment of gasolines and kerosenes, the clay acts as a catalyst (5). In the treatment of heavy oils and of reformer charge stocks, it is used as an adsorbent.

Disposal of spent clays may be a problem, although there is a limited demand for them as raw materials in the manufacture of cinder bricks (31). One refiner mixes spent clays with natural clays at the refinery site to produce fill for construction operations (13).

Stabilization of Cracked Gasolines

At moderate temperatures—300 to 600°F—clays such as fuller's earth and bauxite catalyze the polymerization of the reactive materials that tend to impart color or form gum when cracked gasolines are stored.* The clayed product is rerun to eliminate the polymer. Processes that make use of this property of clays to "stabilize" cracked gasolines include the Gray, the Stratford, and the Osterstrom (37,48), and others have been proposed (30). The catalyst is usually employed in fixed beds of 30–60 mesh material, through which the charge stock is passed as a vapor or as a liquid. In some units, finely divided clay has been circulated through the vaporized charge as a slurry in recycled polymer. The clay-treating reactor has been interposed between the cracking unit and its fractionating column; this arrangement obviates a separate rerunning operation. Typical operating conditions are shown in Table 13-4. Rerun gasoline yields are generally in the range of 98.5 to 99.5 per cent, but they may be as low as 94 per cent with highly cracked stocks (22). Spent clay is

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* The color formers are believed to be cyclic unsaturated compounds, and the gum formers are believed to be aliphatic diolefins and olefins attached to benzene rings (22).

usually not regenerated. As indicated in Table 13-4, clay life ranges from 1,000 to 70,000 bbl per ton.

Table 13-4. Typical Conditions for Clay Treating of Cracked Gasolines (22,41,60)

Process	Process description		Temperature, °F	Pressure, psi	Contact time, sec	Clay life, bbl/ton
	Catalyst	Feed				
Gray	Fixed-bed	Vapor	250–500	5–400	20–400	4,000
Stratford	Slurry	Vapor	230–330	.....	......	1,000
Osterstrom	Fixed-bed	Liquid	500–600	1,000	......	70,000

Desulfurization of Virgin Gasoline*

At temperatures of 650 to 800°F, fuller's earth and bauxite catalyze the conversion of organic sulfides and mercaptans to hydrogen sulfide and hydrocarbons (60). This reaction is used to desulfurize virgin gasolines, virgin sulfur compounds being principally sulfides and mercaptans. The process may also be applied to cracked gasolines, although the sulfur in these stocks is largely thiophenic, and thiophenic sulfur is not affected. The catalyst is employed in fixed beds. Typical reaction conditions are 800°F, 50 psi, and a volumetric space velocity† of 1 (51). Volumetric yields range from 98 to 99.5 per cent of the charge. Removal of sulfur raises the octane number of the product, particularly on a leaded basis. In the case cited, reducing sulfur content from 0.123 to 0.004 per cent raised the clear research octane rating by two units, the leaded (3 cc) rating by seven units.

Under desulfurization conditions, coke deposits slowly on the catalyst and deactivates it. The catalyst can be regenerated by burning the coke off under controlled-temperature conditions. Regeneration temperature is controlled by charging steam with the combustion air. Without regeneration, a ton of bauxite will desulfurize 5,000 to 20,000 bbl of virgin gasoline, 1,200 bbl of cracked gasoline, or 5,000 bbl of kerosene (50,51). With regeneration, a ton will desulfurize 50,000 to 100,000 bbl of virgin gasoline.

Adsorptive Clay Treating

High-surface-area materials‡ such as Attapulgus clay and activated bauxite adsorb asphaltic, resinous, and acidic materials from heavy oils at

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* Processes include the Gray (Gray Process Corp.), Cycloversion (Phillips Petroleum Co.), and Houdry Treating [Houdry Process Corp. (45)].

† Volumetric space velocity = volumes of oil (as liquid) per hour divided by volume of catalyst.

‡ Surface areas are about 13 acres per lb for Attapulgus clay and 24 acres per lb for activated bauxite (43). Montmorillonite clays have also been used as adsorbents.

low to moderate temperatures (24,35,43). This property is utilized to remove traces of asphalts and resins from low-asphalt-content stocks, and thereby to improve their colors. Color stability, oxidation resistance, and demulsibility are also improved. High-asphalt stocks are first acid treated or propane deasphalted, with clay treating often being used as a clean-up operation. Clay treating of acid-treated stocks neutralizes them by removing traces of sludge or acidic materials. Clays are also used to adsorb arsenic compounds from feeds to catalytic reforming (43,55).

Two general types of clay treating are practiced: percolation filtration and contact filtration. In percolation, the liquid charge is passed through fixed or moving beds of Attapulgus clay or activated bauxite, usually 20–60 or 30–60 mesh. In contact filtration, the charge is mixed thoroughly with fine clay (150–200 mesh) and is then filtered; the operation may be either batch or continuous.

Adsorbent Requirements. Adsorbent requirements are greater for darker feeds, and they increase as the permissible color in the product is lowered. Because the amount of color bodies that a clay will adsorb increases with the color of the charge stock, two stocks of different colors can be decolorized with less clay if they are processed separately than if they are combined (35). Fractionating a feed into lighter and darker fractions may reduce clay requirements by as much as 50 per cent (14).

Attapulgus clay may be used to decolorize and neutralize any petroleum stock (43). It is particularly well suited to the removal of high-molecular-weight sulfonates, resins, and asphaltenes. Also, Attapulgus clay is preferred for pretreating feeds to catalytic reformers. Because activated bauxites remove tastes and odors, they are popular for finishing waxes (43). They are also used for finishing oils of high viscosity index, especially residual oils.

Adsorbent usages are lower in percolation units than in contact units because percolation clays are regenerated and reused, whereas contact clays are used once through.

Regeneration of Adsorbents. Adsorbents are regenerated by burning the adsorbate. Because temperatures above 1100°F deactivate adsorbents (43), burning is carried out at controlled temperatures. To achieve control, rotary kilns, multiple-hearth furnaces, and Thermofor kilns are used for regeneration. Although the optimum temperature may be different for each treating operation, it is not practical to segregate adsorbents and they are all regenerated at one temperature—usually 1050°F (32). Because overtreating accelerates deactivation of adsorbents, residence time in the regenerator should be as short as is consistent with complete regeneration. Usual regeneration periods are 10 to 30 min (32).

Rotary kilns are brick-lined cylinders inclined slightly from the horizontal. The slowly revolving kiln is fired from the lower end, clay being charged to the upper end. Kilns range from 2.5 to 6 ft in diameter and from 24 to 60 ft in length, and their regeneration capacities are usually between 24 and 48 tons per day (44).

Multiple-hearth furnaces are similar to the furnaces used in roasting ores (44). They are cylindrical vessels divided into compartments by hearths, approximately horizontal and so arranged that clay brought in at the top flows across each hearth as it passes down through the tower. On each hearth, clay movement is facilitated by rabble arms attached to a rotating central shaft. Combustion air passes through the vessel, countercurrent to the flow of clay. Multiple-hearth furnaces range from 16 to 25 ft in diameter and contain from 7 to 12 hearths. Regeneration capacities range from 24 to more than 100 tons per day. When natural gas or refinery gas is used as fuel, about 1,000 cu ft are required per ton of clay (44).

Thermofor kilns (64) are stationary chambers containing cooling tubes, through which a molten salt is circulated at a temperature of about 1000°F. Because Thermofor kilns control temperatures best, they deactivate clays less than do other regeneration systems; consequently, clay life is longer when Thermofor kilns are used (43).

Percolation in Fixed Beds. The original clay-treating process—fixed-bed percolation—dates back to about 1850. Its operation is semicontinuous. Clay is charged batchwise to a vertical cylindrical vessel, and then oil is passed through it until the clay is spent.* Like all fixed-bed units, a percolator contains many contacting stages. Because the first increment of feed is exposed to clean adsorbent in all the stages, the color of the first effluent is very light. As the clay gradually becomes saturated, the effluent gradually darkens. When its color reaches a limiting value, the oil charge is interrupted, and the bed of clay is allowed to drain. Next a paraffinic heavy naphtha is sent through the bed to displace the oil held up in the bed, after which the adsorbent is steamed to recover the naphtha. Spent clay is then removed from the percolator and sent to a kiln where the adsorbed materials are burned off at controlled temperatures.

The liquid holdup in the pores of the adsorbent and in the interstices of the bed equals about 70 per cent of the bulk volume. When the bed is drained at the end of a cycle, 40 to 50 per cent of the holdup is recovered. The quality of this material is equal to or better than the feed stock, and it is recycled. The first portion of the oil recovered by naphtha washing is also of good quality and is usually recycled after being fractionated from the naphtha. In a typical case, the recycle material constitutes about 70 per cent of the holdup volume (43).

* Initially, the feed is charged slowly to fill the vessel; when the vessel is filled, it may be allowed to soak for a period before more oil is charged (43).

Preferred dimensions for percolators are height-to-diameter ratios of 3 to 4; small-diameter vessels, however, should have a bed depth of at least 15 ft (43). Most percolators are 5 to 15 ft in diameter and 15 to 30 ft high; they contain 10 to 60 tons of clay or twice as much bauxite (24,32,35). Operating temperatures range from about 100 to about 250°F, higher temperatures being used with more-viscous stocks. Oil usually flows downward, although upward flow is claimed to give better results by eliminating channeling. Flow rates must be slow enough to permit diffusion into the adsorbent to occur. Maximum permissible flow rates have been related to the viscosity of the fluid and the particle size of the adsorbent by the empirical equations (28,43):

$$R_x = R_0 \frac{0.0101 - D_p}{0.008}$$

$$\log R_0 = 0.0385 - 0.0387\mu$$

where R_x = maximum permissible flow rate, vol/vol/hr
R_0 = maximum permissible flow rate when $D_p = 0.0021$ ft
D_p = mean equivalent spherical diameter of the adsorbent, ft
μ = viscosity of the fluid, centipoises

Pressure drops are calculated by standard equations for laminar flow (43).

Because the adsorptive capacities of Attapulgus clays drop with each regeneration, such clays are segregated according to the number of regenerations, and the freshest are used for the most difficult treatments.* Clays may be reused 10 to 20 times (24). Activated bauxite also loses activity with use, but so slowly that replacement of mechanical losses (1 to 2 per cent per regeneration) maintains the activity at a satisfactory level.

Treating capacity, between regenerations, varies with the feed stock and the adsorbent used; typical figures are 7 to 20 bbl per ton (24). Dilution of the feed with a naphtha increases the permissible oil throughput, presumably because the naphtha holds in solution colorless aromatic materials that would otherwise be adsorbed (43). Some representative operations are shown in Table 13-5 for lubricating oils, and in Table 13-6 for waxes, and typical material balances are given in Table 13-7. Percolation costs range between 0.4 and 5 cents per gal of product (28,43).

Plant designs should be based on experimental data (43). Some design factors are listed in Table 13-8.

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* Percolation clays and bauxites contain both bound and free water as they are delivered to the refiner. Before they are used the first time, they are "tempered" by passage through the regenerator to drive off free water and part of the bound water (43). Tempering temperatures are 500 to 800°F for clays, 700 to 900°F for bauxites, and exposure times are 15 to 30 min.

Continuous Percolation. The moving-bed principle (Chap. 5) has been applied to percolation* (43,56). Unlike other moving-bed applications in petroleum refining, continuous percolation involves the contacting of a liquid with a solid. Regenerated adsorbent, about 15–30 mesh, passes down through a percolation vessel countercurrent to the charge. From the bottom of the percolator, spent clay is transferred to a wash tower, either as a slurry (56) or as a drained adsorbent, the draining occurring in a screw drive that elevates the spent catalyst above the liquid level in the percolator (43). In the wash tower the clay again passes down, countercurrent to a paraffinic naphtha wash stream. Washed clay is then dried as a fluidized bed (57) by indirect exchange with steam. Elevators carry the dry clay to and from a regeneration kiln. Lower clay requirements and lower oil losses are claimed (56). Clay requirements are reduced by 10 to 35 per cent (43,56).

Table 13-5. Typical Operations in Clay Treating of Lubricating Oils (43)

Feed stock						Treatment			
Crude-oil source	Prior processing[a]	Gravity, °API	Viscosity, SSU		Color, NPA	Adsorbent	Temp., °F	Bbl/ton[b]	Product color, NPA
			100°F	210°F					
Louisiana	*E, D*	33.6	158	45.7	5	Clay, AA	160	68	1½
Pennsylvania	*D*	30.4	178	45.3	4½	Clay, AA	160	135	3
West Texas	*E, D*	32.7	209	47.4	1¼	Clay, AA	180	257	1
California	*E, D*	28.9	326	51.5	4 dil.	Clay, AA	180	157	4
California	*E, D*	28.9	326	51.5	4 dil.	Clay, A	180	152	4
California	*E*	22.7	457	53.2	3¾ dil.	Clay, AA	180	19	4
California	*E*	'22.7	457	53.2	3¾ dil.	Clay, A	180	16	4
Iraq	*E, D*	28.1	457	60.8	7¼	Clay, AA	160	160	3
Illinois	*E, D*	29.0	512	62.6	4¼	Clay, AA	180	52	2
West Texas	*P, E, D*	26.6	1618	119.3	7+	Clay, AA	180	63	6
California	*V, E, D*	26.0	1846	120.2	4½−	Clay, AA	180	555	4
East Texas	*P, E, D*	25.6	1710	121.0	8 dark	Clay, AA	210	51	5
East Texas	*V, E, D*	26.3	....	147.0	5¾	Clay, A	210	61	4¾
East Texas	*V, E, D*	26.3	....	147.0	5¾	Clay, AA	210	75	4¾
Iraq	*P, E, D*	24.3	2948	162.5	7¼	Clay, AA	180	68	5
North Louisiana	*E, D*	28.0	207	46.5	2−	Bauxite	...	48	1½
West Texas	*E, D*	32.7	209	47.4	1¼	Bauxite	...	151	1
California	*E, D*	28.9	326	51.5	4 dil.	Bauxite	...	65	2
Iraq	*E, D*	28.1	457	60.8	7¼	Bauxite	...	130	3
Oklahoma	*E, D*	29.1	512	62.6	4¼	Bauxite	...	114	2
East Texas	*P, E, D*	27.7	1116	92.4	8	Bauxite	...	23	4
East Texas	*P, E, D*	27.4	1678	117.3	5¼	Bauxite	...	47	5
West Texas	*P, E, D*	26.6	1618	119.3	7−	Bauxite	...	60	6

[a] *P* = propane deasphalting, *V* = vacuum distillation, *E* = extraction, *D* = dewaxing.

[b] Basis: new clay. With regenerated clays the equivalent barrels per ton would be less.

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* By the Socony-Mobil Oil Co. (45) and by Minerals and Chemicals Corp. (43).

Table 13-6. Typical Operations in Clay Treating of Waxes (43)

Feed stock						Treatment			Product color	
Crude-oil source	Gravity, °API	Viscosity SSU, 210°F	M.P., °F	Color		Adsorbent	Temp., °F	Bbl/ton	Saybolt	NPA
				Saybolt	NPA					
Paraffin waxes										
Pennsylvania........	45.2	36.7	124	12	......	Bauxite	180	147	21	
Wyoming...........	43.4	37.2	125	8	......	Bauxite	180	58	26	
East Texas..........	38.7	39.6	134	...	¾	Bauxite	210	32	30	
Oklahoma...........	37.6	37.3	123	...	1+	Bauxite	180	18	25	
Oklahoma...........	37.6	37.3	122	...	1+	Clay	180	11	25	
Oklahoma...........	41.0	36.2	122	9	......	Bauxite	180	85	25	
Illinois.............	42.3	41.4	131	...	2¾	Bauxite	180	37	20	
Illinois.............	42.3	41.4	131	...	2¾	Clay	180	33	20	
California...........	38.5	40.7	143	...	½	Bauxite	200	250	30	
California...........	38.5	40.7	143	...	½	Clay	200	331	30	
Petrolatums and microcrystalline waxes										
Pennsylvania........	31.0	93.6	132	...	5¾ dil.	Bauxite	180	1.1	...	½
Pennsylvania........	32.9	93.4	128	...	4+	Bauxite	180	1.8	...	½
Pennsylvania........	31.0	93.6	132	...	5¾ dil.	Bauxite	180	2.1	...	½
Pennsylvania........	32.9	93.4	128	...	4+	Bauxite	180	2.4	...	½
East Texas..........	31.8	74.5	167	...	7	Bauxite	210	21.6	...	1
California...........	35.7	50.3	159	...	2¾	Bauxite	210	105.2	18	
Illinois.............	35.4	77.0	169	...	5½	Bauxite	210	17.0	...	1
Oklahoma...........	31.9	77.6	185	Black		Bauxite	250	6.3	18	
Oklahoma...........	31.9	77.6	185	Black		Bauxite	250	11.4	...	1
Mid-Continent......	30.6	82.3	175	Brown		Bauxite	210	7.0	...	½
Mid-Continent......	30.6	82.3	175	Brown		Bauxite	210	15.9	...	1¾

Table 13-7. Typical Material Balances for Fixed-bed Percolations (43)

	Flows, bbl, per 100 bbl of fresh feed for cycles of indicated length (bbl/ton)			
	10	50	75	100
Charge....................	100.0	100.0	100.0	100.0
Recycle..................	20.4	4.1	2.6	2.0
Total.................	120.4	104.1	102.6	102.0
Drainage (recycle).........	9.9	2.0	1.3	1.0
Wash-oil recycle...........	10.5	2.1	1.3	1.0
Wash-oil discard..........	4.2	0.9	0.6	0.5
Steamings.................	5.5	1.2	0.7	0.6
Loss to adsorbent..........	2.6	0.6	0.4	0.3
Product..................	87.7	97.3	98.3	98.6

Treating temperature depends upon the viscosity of the charge stock (57). Less-viscous stocks may be treated at ambient temperatures. More-viscous stocks are heated to reduce their temperatures to 5 centipoises or less; for heavy oils, temperatures as high as 350°F are used. Oil throughputs are 10 to 20 bbl per day per sq ft of cross-sectional area, and adsorbent bed heights are about 17 ft. From 0.4 to 0.7 vol of wash naphtha are used per volume of adsorbent circulated.

Table 13-8. Typical Design Factors for Fixed-bed Clay Percolators (28,43)

Bulk density of adsorbent, lb/cu ft:	
Attapulgus clay	34–36
Activated bauxite	60–63
Voids in beds, %	38–45
Bed depth, minimum, ft	15
Bed height/diameter ratio, minimum	3
Flow rates:	
Feed, filling the vessel, vol/vol/hr	0.25
Feed, normal operation	See text
Wash naphtha, vol/vol/hr	0.25
Steam usage (steaming), lb/ton of adsorbent	800–1,500
Time allowances, hr:	
Charging adsorbent	3–4
Soaking, after filling vessel with feed	1
Draining	6–8
Steaming ($A \times$ lb of adsorbent in bed); $A =$	0.004
Dumping	4
Regeneration conditions:	
Temperature, maximum, °F	1,100
Time, min	10–30

Contact Filtration.* Contact filtration was introduced about 1920, the first operations being batch clean-up operations following acid treating; acid treating and claying were carried out sequentially in the same equipment. Later units contain separate facilities for the two steps, and they operate continuously (16,24,52). Finely divided clay (0.1 to 1 lb/gal) is slurried into the charge stock, and the slurry is heated to a temperature in the range of 225 to 600°F, the higher temperatures being used with more-viscous oils. Heated slurry is passed through a "contact tower," which is sized to give the desired reaction time—generally ½ to 1 hr. The slurry is then cooled and filtered continuously. To facilitate filtration, a naphtha diluent may be added to the slurry before the filtration step.

When clay treating is used to neutralize acid-treated oils, the clay should contain little calcium, magnesium, or iron, any of which could react to form oil-soluble soaps (24).

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* Developed by the Filtrol Corp. (45).

Comparative Costs. Although clay requirements for continuous contacting are greater than for fixed-bed percolation, investment costs are lower and continuous contacting is usually preferred over fixed-bed percolation for new installations. It is claimed (12) that the investment for moving-bed percolation is only about 20 per cent higher than for continuous contacting and that the incremental investment is paid off rapidly by operating savings. It is further claimed that operating savings are sometimes sufficient to permit retiring a continuous contact plant.

HYDROGEN TREATING*

Hydrogen treating is mild hydrogenation that removes sulfur, nitrogen, oxygen, and halogens from a feed and converts diolefins to olefins. It may also saturate olefins. Stocks ranging from light naphthas to lubricating oils are hydrogen treated. Pressures usually range between 400 and 1,000 psi, although lower pressures are also used. Temperatures are between 400 and 750°F and liquid yields are usually 100 vol per cent, or slightly higher.

Charge Stocks to Reforming. The major application of hydrogen treating has been removing sulfur from feeds to catalytic reformers. As discussed in Chap. 8, low sulfur contents are required to avoid corrosion problems in reformers, unless the high-temperature equipment is made of 18-8 steel or is aluminized. Nitrogen, oxygen, halides, and trace metals are also removed, and olefins in cracked stocks are hydrogenated. Operating pressures are usually 200 to 500 psi. For virgin stocks, hydrogen consumptions are about 5 scf per bbl for each 0.1 per cent sulfur removed.

Cracked Gasolines. Cracked gasolines may be hydrogenated lightly to eliminate diolefins and thus improve stability (3,24,26) or they may be treated more severely to reduce their sulfur contents also (1,3,8,36,68).

Diolefins are hydrogenated readily, but some olefins are converted at the same time. To minimize octane losses, the minimum conversion of olefins is desirable. With a nickel-tungsten-sulfide catalyst, best results were obtained when about 900 scf of hydrogen-rich gas were charged per barrel of feed (about a 1/1 molar ratio), and lower temperatures gave more selective conversions (26). Pressure per se did not affect rates of reaction except as it affected contact time. Conditions employed experimentally were 40 to 200 psi and 400 to 550°F, and the liquid hourly space velocity was 3 to 18 vol per vol of catalyst. On a stock with a bromine number† of 43 and a sulfur content of 0.11 per cent, desulfurization counteracted

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* For a general discussion of hydrogenation, see Chap. 12.

† Bromine number is a measure of olefin content. It is expressed as the number of grams of bromine absorbed per 100 grams of feed. One olefin molecule reacts with two bromine atoms.

the saturation effect on leaded research octane ratings at olefin conversions below 30 per cent, and the products rated equal to or slightly better than the feed. At higher conversions of olefins, the leaded ratings were reduced.

When a cracked gasoline is desulfurized by hydrogenation (1,19,36), saturation of olefins lowers its clear octane ratings appreciably, but improved response to tetraethyllead compensates for most of the loss, except at very high sulfur reductions. Because olefins concentrate in the light portion of gasoline and sulfur concentrates in the heavy portion, it is usually desirable to process only the heavy stock* (11,36). With some catalytic gasolines, most of the sulfur is contained in the fraction boiling above 360°F (36). With such gasolines, 80 per cent desulfurization of the total gasoline may be achieved by hydrogen treating only the heaviest portion, with no loss in clear octane ratings, and with some gain in leaded ratings.

If contact time is held constant, hydrogenation of olefins is unaffected by pressure (36). Desulfurization, on the other hand, is faster at lower pressures (3,8,36). Thus, cracked gasolines should be desulfurized at the lowest pressure at which satisfactory catalyst life can be achieved. A pressure of 300 psi has been suggested for a cobalt-molybdena catalyst (36).

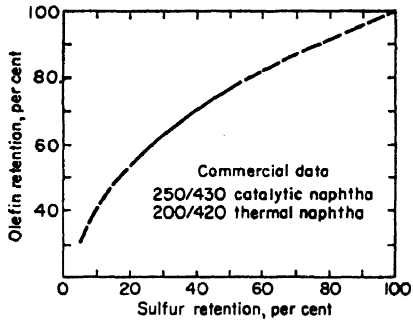

FIG. 13-6. Olefin and sulfur retentions in the hydrogenation of cracked gasolines (1).

The relationship between olefin retention and sulfur retention is shown in Fig. 13-6 for heavy cracked gasolines treated over a tungsten-nickel-sulfide catalyst at 500 to 750 psi (1). Octane effects are shown in Figs. 13-7 and 13-8. Although the products are not doctor sweet, they are usually odor sweet.† Gum contents are consistently low, for example, 1 mg per 100 cc. Cycle lengths, between regenerations, are two to four months, and catalyst usage is about 1 lb per 600 bbl of feed. Hydrogen consumptions are 6 to 8 scf per bbl per unit of bromine-number reduction and 50 to 100 scf per bbl per per cent of sulfur removed (6).

Under some circumstances, hydrogen-treating plants for desulfurizing cracked naphthas can be justified to retire acid-treating units (1).

Distillate Fuels. Hydrogenation upgrades distillate fuels. In addition to removing sulfur, the operation improves odor and color properties,

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* Also, the selectivity for desulfurization over olefin saturation is lower for lighter stocks (11).

† Gasoline sweetness is discussed in Chap. 14.

burning qualities, and cetane numbers, the latter by one to six units (38,42,72). At present, distillate fuels account for the second largest portion of hydrogen-treating feeds, after reformer charge stocks. For virgin stocks, hydrogen consumption is 50 to 150 scf per bbl for each per cent of sulfur removed (63,67).

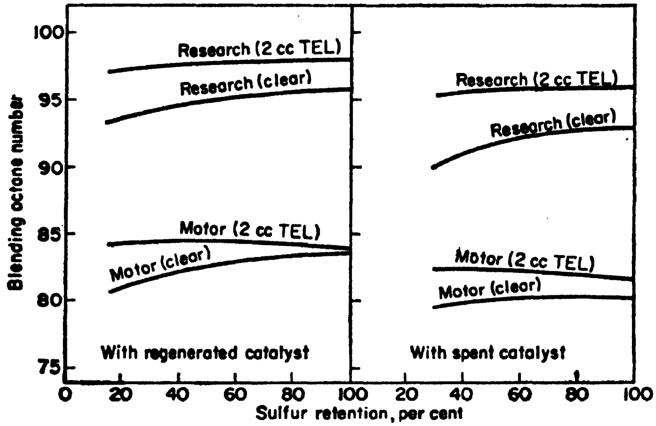

FIG. 13-7. Octane effects in the desulfurization of a catalytic naphtha containing 0.5% sulfur (1).

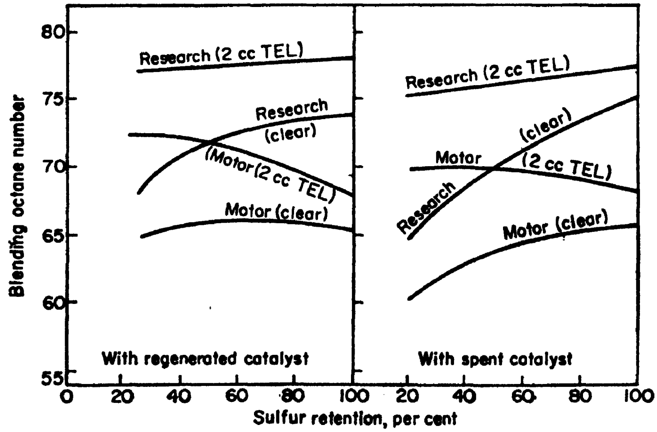

FIG. 13-8. Octane effects in the desulfurization of a thermal naphtha containing 1.15% sulfur (1).

More severe conditions are sometimes employed to saturate part of the aromatics and thus effect a further improvement (25,72).

Gas Oils. Mild hydrogenation of a virgin or coker gas oil reduces its sulfur content, and, consequently, the sulfur contents of the products obtained from cracking it. The cracking properties of the feed are also improved, more gasoline and less coke being made from a hydrogenated feed (4,39,71). The effects of these operations are discussed in Chap. 7.

Lubricating Oils and Waxes. Lubricating oils and waxes are hydrogen treated to improve color and odor properties (29,38). Acidic materials are almost completely eliminated, and sulfur and carbon residue are reduced. Viscosity index of a lubricating oil is improved slightly, but pour point is raised as much as 10°F. Waxes are hydrogenated at about 450°F (9).

SODIUM TREATING

Finely divided sodium is a versatile treating agent for removing reactive compounds from petroleum stocks (69). At about 70°F, it reacts only with compounds having active hydrogens—phenols and mercaptans, for example. At temperatures of about 400°F, sodium reacts with sulfur compounds to form sodium sulfide. At intermediate temperatures, it reacts with diolefins and reactive olefins such as styrene. No commercial applications of sodium treating have been reported.

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CHAPTER 14

SWEETENING AND MERCAPTAN EXTRACTION

Sulfur is undesirable in gasolines and distillate fuels. Hydrogen sulfide and mercaptans are especially undesirable because they have objectionable odors, even in very low concentrations. Any hydrogen sulfide that may remain after distillation is readily removed by caustic washing. Caustic washing also removes some lower-boiling mercaptans, which are weak acids whose acidities fall off rapidly as molecular weight is increased. Lower-boiling mercaptans are extracted readily, but the higher-boiling ones are not. Consequently, mercaptans are often converted into disulfides, which are practically odorless, by one of a number of "sweetening" processes. By definition, a stock is sweet if it passes the doctor test.* This test is sensitive to about four parts of hydrogen sulfide or mercaptan sulfur per million parts (9). It has been claimed that the test is too severe for gasolines—that 50 ppm would be satisfactory in most cases and that 20 ppm† should always be satisfactory (9). Because they are sometimes stored indoors in open containers, No. 1 fuel oils are always sweetened. Some No. 2 fuel oils are marketed sour.

Because sulfur compounds lower the octane number of a leaded gasoline, mercaptan-rich stocks are sometimes extracted to remove the bulk of the mercaptans prior to sweetening. Acid treating, clay treating, and hydrogen treating, which are discussed in Chap. 13, also remove or destroy mercaptans.

SWEETENING

The principal sweetening processes include doctor, copper chloride, air-inhibitor, and air-solutizer processes. Hypochlorite sweetening is also used for special purposes, and a lead sulfide process has been used to some extent (6). Various others have been proposed (11,24).

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* The test sample is shaken with an equal volume of a sodium plumbite solution and a small amount of sulfur. If no dark discoloration forms at the interface, the sample is sweet.

† Caustic-washed gasolines are said to be "odor sweet" when their mercaptan contents are reduced to 10 to 20 ppm (12).

With the exception of the lead sulfide process, the over-all reactions are the same in all processes:

$$2RSH + (O) \rightarrow R_2S_2 + H_2O$$

The oxygen may be supplied either as molecular oxygen or in an oxidizing agent. In the latter cases, air is usually used to regenerate the oxidizing agent. In the Bender process, sulfur is substituted for oxygen, and hydrogen sulfide is a product instead of water.

Doctor Sweetening

The doctor process was developed first, and it is still widely used. Its advantages include versatility, ease of operation, and use of a cheap reagent. Its principal disadvantage is a slight increase in product sulfur contents. In gasolines, such an increase has an adverse effect on octane ratings; in distillate fuels, it may lower burning quality. Consequently, doctor sweetening is being superseded by other processes, especially for treating gasoline.

Chemistry. Doctor sweetening converts mercaptans to disulfides by treatment with sodium plumbite dissolved in caustic soda.* Although the chemistry is quite complex (8,24), the over-all sweetening reactions may be represented by

$$\begin{gathered} 2RSH + Na_2PbO_2 \rightarrow Pb(RS)_2 + 2NaOH \\ Pb(RS)_2 + S \rightarrow PbS + RSSR \end{gathered}$$

Some sulfur also reacts to form polysulfides. For example,

$$Pb(RS)_2 + 2S \rightarrow PbS + RSSSR$$

Some polysulfides form even when sulfur usage is less than the theoretical requirement for converting mercaptans to disulfides.

Lead sulfide is converted back to sodium plumbite by air blowing the solution:

$$\begin{aligned} &PbS + 2O_2 \rightarrow PbSO_4 \\ &PbSO_4 + 4NaOH \rightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O \end{aligned}$$

Because the presence of sodium sulfate reduces the solubility of lead sulfate, a portion of the solution must be discarded periodically to control buildup of sodium sulfate.

Discarded doctor solution may be regenerated (11,24) by settling to separate an emulsion of caustic, oil, and lead sulfide from a top oil phase

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* Doctor solution is made by saturating an 8 to 24 per cent solution with lead oxide (15). An 8 per cent solution dissolves 1 per cent lead oxide; a 24 per cent solution dissolves 3 per cent.

and a bottom sodium plumbite phase; breaking the emulsion by heating it to about 150°F; and separating a slurry of lead sulfide and air blowing it at 175°F for as long as 43 hr at atmospheric pressure. (Shorter times are permissible at higher air pressures.) The regenerated solution may be washed with oil to decolorize it.

Hydrogen sulfide, organic acids, and phenols react with caustic to form sodium salts. To prevent build-up of such salts in the doctor solution, the feed is usually prewashed with caustic or with spent doctor solution.

Operations. Doctor sweetening is carried out either continuously or batchwise. In continuous operations, a solution of sulfur of known strength is metered into the feed. The total feed is then contacted with doctor solution in one or two stages (19,27). When two stages are used, make-up doctor solution is added periodically to the second stage, from which it displaces an equal amount of the circulating solution. The displaced solution is sent to the first stage, and an equal portion of first-stage solution is sent to regeneration or discard. Spent doctor solution is regenerated continuously by circulating it through a regenerator, where it is contacted with air. A schematic diagram of a single-stage plant is shown in Fig. 14-1.

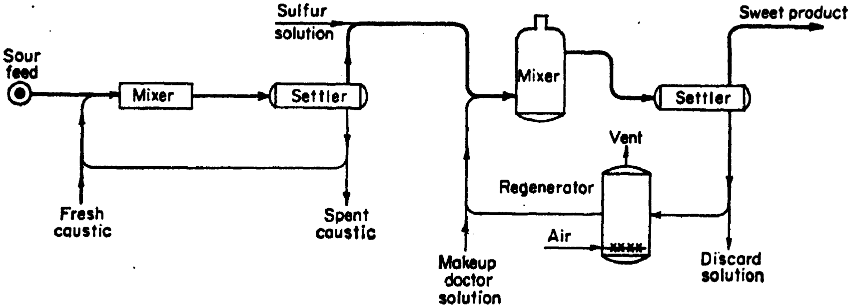

FIG. 14-1. Doctor sweetening.

Operating Conditions. Doctor sweetening is carried out at about 150°F. In a single-stage operation, about 20 parts of doctor solution are circulated per 100 parts of feed. Feed and doctor solution are contacted for about 30 sec before the sulfur-containing slip stream is added, and the total mixture is then stirred for 5 to 15 min (27). Because lead sulfide precipitates as very small particles if only the theoretical amount of sulfur is used, a slight excess is employed in treating distillate fuels. The excess reacts to form polysulfides. Inasmuch as polysulfides reduce the octane rating of a gasoline and lower the burning quality of a distillate fuel, sulfur additions must be carefully controlled.

Typical conditions for air regeneration of doctor solution are 180 to 230°F and 15 to 100 psia (27).

Copper Chloride Sweetening*

Copper chloride sweetening has the advantage over doctor sweetening of requiring no sulfur. The copper chloride catalyst may be employed as a fixed bed, as a slurry, or as a solution (20). Because corrosion problems have limited the use of the solution technique (27), only the other two will be discussed here.

Chemistry. In simplified form, copper chloride sweetening reactions are

$$4RSH + 4CuCl_2 \rightarrow 2RSSR + 4HCl + 4CuCl$$
$$4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$$

Over-all, the reactions are

$$4RSH + O_2 \rightarrow 2RSSR + 2H_2O$$

An excess of oxygen (1.5 to 3 times the theoretical) is used to obviate incomplete regeneration, which would have an adverse effect on the gum content and the inhibitor response of the product (27). In some cases, this practice results in the formation of peroxides.

A small amount of water is formed in the sweetening reaction. In the fixed-bed and slurry processes, the water must be removed as it forms; otherwise it will accumulate in the catalyst and interfere with the operation. One method of removal is to heat the feed to a temperature high enough that the water of reaction dissolves in the product stream (9). Reaction temperature is raised approximately 1°F for each unit increment of mercaptan number† of the feed stock.

Operations. In copper chloride sweetening, the feed is prewashed with caustic to remove hydrogen sulfide. It is then coalesced to remove traces of caustic, warmed, and charged to a slurry or fixed-bed reactor.

A flow diagram for a slurry plant is shown in Fig. 14-2. After caustic washing, coalescing, and warming, the feed is mixed with air or with oxygen and then with a slurry of copper chloride (one part) and clay (four parts). The mixture is sent to a reactor-separator, from which catalyst is recycled to the feed. Treated product may be water-washed before it is withdrawn from the system. In a fixed-bed plant, air is mixed with the feed, and the mixture is passed downflow over a bed of catalyst.

Reaction temperatures are between 80 and 120°F (27). At lower temperatures, the reactions are slow; at higher temperatures there are undesirable side reactions.

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* Copper chloride sweetening processes have been developed by Phillips Petroleum Co., Universal Oil Products Co., Linde Air Products Co., and by Air-Reduction Sales Co.

† Mercaptan number is expressed as milligrams of mercaptan sulfur per 100 ml of sample.

Because copper catalyzes the deterioration of gasoline, even minute amounts must be removed or deactivated. Water washing does not remove all the copper, and sodium sulfide or zinc sulfide washes are sometimes used, particularly with cracked stocks. Chelating agents are always added to the final product to sequester residual copper and deactivate it.

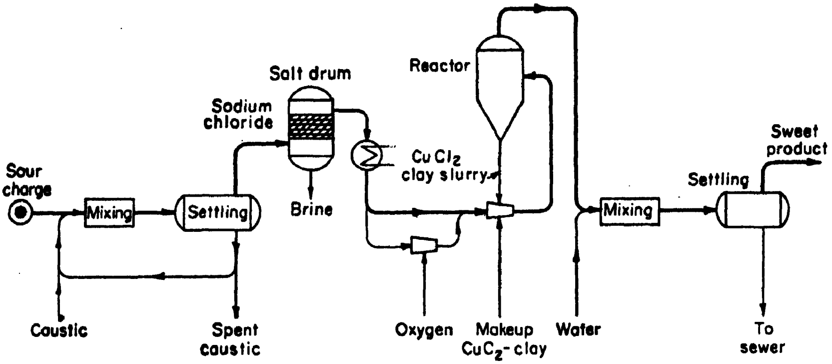

FIG. 14-2. Copper chloride sweetening—slurry process.

Feed Stocks. Copper chloride processes may be used to sweeten butanes, gasolines, kerosenes, and heating oils (20), but some kerosenes are not susceptible (18). In one such case, the kerosene responded to copper chloride after it was solvent-extracted.

Copper chloride sweetening works best on virgin stocks. It does not work well on stocks containing tertiary mercaptans, which react very slowly (27). Feeds containing nitrogen bases do not respond well either, and they are not usually copper sweetened.

Air-inhibitor and Air-solutizer Processes

Gasolines can be sweetened without the use of chemical oxidants. The processes employed are called air-inhibitor and air-solutizer processes. Air-inhibitor sweetening is limited to cracked stocks, especially light, catalytically cracked gasolines; air-solutizer sweetening is applicable to all gasolines (12,27). As with other sweetening processes, charge stocks to these processes are prewashed to remove acidic materials.

Air-inhibitor Sweetening. In an air-inhibitor plant, phenylene diamine inhibitor is added to the prewashed gasoline, which is then mixed with air and caustic in a line mixer. Caustic is settled away from the gasoline, which is allowed to stand in storage to complete the sweetening reaction. Some peroxides form, and the gum content of the gasoline is increased (27). Addition of a small amount of doctor solution to the caustic speeds up the reaction, and markedly reduces the formation of peroxides and gum (21). (Reducing the peroxide raised the octane number of the leaded product—in one example by about 0.6 unit.) For best results, the gasoline should be in contact with caustic until sweetening is complete. Treating temperatures are 80 to 120°F, and caustic (10 to 40°Bé) is circulated at the rate of about 0.1 vol per vol of feed (27). In one case, 7.5 lb of inhibitor were used per 1,000 bbl of feed, and 1 per cent of the theoretical amount of doctor solution was used (21). The loss of inhibitor in the operation ranged from almost none to a few pounds per 1,000 bbl of feed.

Air-solutizer Sweetening. Air-solutizer sweetening is very similar to the air-inhibitor process, except that potassium hydroxide may be used rather than caustic, and solutizing agents, such as methanol or cresylic acids, are added to the solution to increase its capacity for dissolving mercaptans. Thorough mixing for 2 to 20 min is required. The product is sweet as it leaves the mixer, and no peroxides are formed in the operation (22,27).

Other Sweetening Processes

Hypochlorite sweetening is used for sweetening natural gasolines and solvent naphthas and for removal of trace mercaptans from cracked gasolines (26). The charge stock is first caustic-washed to remove hydrogen sulfide, which otherwise would be converted to corrosive sulfur in the process. The caustic-washed material is then treated with sodium or calcium hypochlorite solution to oxidize mercaptans to disulfides:

$$2RSH + NaOCl \qquad R_2S_2 + H_2O + NaCl$$

Traces of acid chlorides are formed, which are dissolved in the oil phase. These are removed by washing with caustic or with water.

Hypochlorite solution is used only once, the spent solution then being used for caustic washing. The solution may be prepared by adding chlorine to 10 per cent caustic—about 5.5 lb of chlorine per barrel of caustic—and it is maintained alkaline at from 0.5 to 3 grams of free caustic per liter of solution (11). If less caustic is used, there is danger of chlorinating the charge stock; if too much is used, the reaction rate may be too slow to be practical.

The effectiveness of hypochlorite as a sweetening agent goes down as the boiling point of the feed stock increases (11); consequently, the process is not employed for the sweetening of distillate fuels.

The Bender* lead sulfide process (1) is used to sweeten kerosenes (6). The basic reaction is

$$2RSH + S \rightarrow RSSR + H_2S$$

The hydrogen sulfide product must be neutralized as it forms; ammonia or sodium hydroxide is the neutralizing agent.

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* Developed by Sinclair Refining Co.

Feed containing sulfur (dissolved in a slip stream) is mixed with a small amount of ammonium hydroxide or caustic and passed over a fixed bed of lead sulfide catalyst at velocities up to 1 ft per min (28). Channeling considerations limit charge rates to 75 bbl per hr per treater. If greater throughputs are desired, parallel treating towers must be used (6).

A modified lead sulfide process (2) has also been used for sweetening virgin and cracked gasolines, kerosenes, and heating oils (4,28). In the modified process some air or oxygen is charged with the feed stock, and a part of the mercaptans react to form water rather than hydrogen sulfide. To avoid the conversion of the lead sulfide catalyst to inactive lead sulfate, the oxygen supplied is held below 30 per cent of the requirement for complete sweetening (2).

MERCAPTAN EXTRACTION

Processes to extract mercaptans from gasoline resulted from the development of tetraethyllead. Because all sulfur compounds reduce the effectiveness of TEL, there is a substantial incentive to remove mercaptans from gasoline rather than to convert them to disulfides (7,16). Typical octane effects are shown in Table 14-1. Extraction is said to be always economical at mercaptan-sulfur levels above 0.05 wt per cent, and it may be economical at levels as low as 0.01 wt per cent (7).

Table 14-1. Octane Improvements from Extraction of Mercaptans (7)

	Type of gasoline		
	Virgin	Virgin-thermal	Catalytic cracked
Distillation, °F:			
10%	125	126	133
50%	158	172	216
90%	226	246	352
RVP, lb	9.6	10.0	8.2
Mercaptan sulfur, wt %:			
Feed	0.052	0.036	0.011
Product	0.002	0.002	0.002
Research octane number, 3 cc TEL:			
Feed	85.5	87.3	96.6
Product	87.3	88.8	97.0

A circulating stream of caustic was first used to extract mercaptans, the caustic being regenerated by steam stripping. Because of limited solubility of the higher-molecular-weight mercaptans, caustic extraction was limited to 40 to 80 per cent mercaptan removal, the exact volume depending upon the particular feed stock. Subsequently it was found that potassium hydroxide is more effective than caustic and that the addition of certain chemicals markedly increases the solubility of mercaptans and thus extends the range of extraction (29). Four commercial processes employing solutizing agents are now in operation (7,15,19,23), as indicated in Table 14-2. In all four processes the extractant is regenerated continuously.

Table 14-2

Process	Solutizing agent	Base
Solutizer (Shell)................	Fatty acids or cresols[a]	22% KOH
Mercapsol (Pure Oil)..........	Salts of acid oils	NaOH
Unisol (UOP)..................	Methanol	NaOH
Dualayer (Magnolia)..........	Cresols[a]	50% KOH

[a] Extraction feed stocks often contain enough cresols for the operation. In such cases only caustic is charged to the system; the cresols are extracted into the circulating caustic until they build up to an equilibrium concentration.

Certain acidic constituents in the feed stocks react with caustic irreversibly; these include hydrogen sulfide, carboxylic acids, and orthothiocresols. To remove these materials, feed stocks are usually prewashed with caustic, in one or two stages, before being charged to the extraction system (7,16). The prewash also removes some mercaptans and cresols If the spent prewash solution is rich in cresols, it may be sold for its chemical content (10).

Extraction

Extraction of mercaptans depends upon the type, amount, and concentration of the base used as extractant, the nature and concentration of the solutizing agent, the number of stages, and the mercaptan content of the regenerated solution (which is a function of the regeneration operation). Extraction is carried out at 80 to 130°F (17,27).

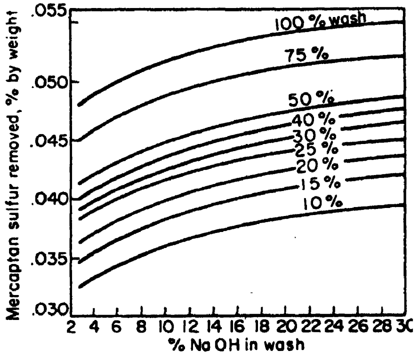

FIG. 14-3. Effects of caustic usage and strength on extraction of mercaptan (11).

Extractants. Both potassium hydroxide and sodium hydroxide are used as extractants. The choice is between higher capacity for potassium hydroxide and lower cost for sodium hydroxide. As illustrated in Fig. 14-3, increasing usage and increasing concentration favor extraction. Although concentration has little effect above 10 per cent when solutizers are not used, concentrations as high as 50 per cent are beneficial in conjunction with solutizers (3).

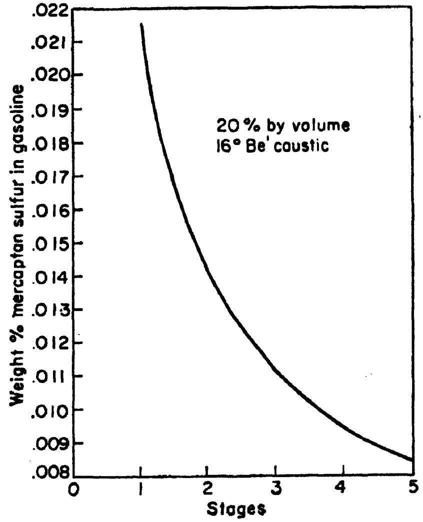

FIG. 14-4. Effect of staging on extraction of mercaptans (11).

Viscosity increases as the concentration of the extractant increases, and separation from treated gasolines becomes more difficult. Separation is said to be very good when the viscosity is 12 centistokes at 100°F and to be satisfactory at 150 centistokes (7).

Staging. Figure 14-4 shows the effects of staging. Substantial improvements are obtained by staging, at least up to five theoretical stages. Two or three theoretical stages are often used commercially (3,7,14,27).

Solutizing Agents. Materials used as solutizing agents include methanol, cresols, and salts of fatty acids. How two of them function is shown in Fig. 14-5. When a solutizer is present, extraction coefficients for all mercaptans are increased, and the effect is most pronounced for the less-extractable, higher-boiling mercaptans. Even with solutizers, however, the higher-boiling mercaptans are extracted much less readily than the lower-boiling. Because cracked stocks contain a higher proportion

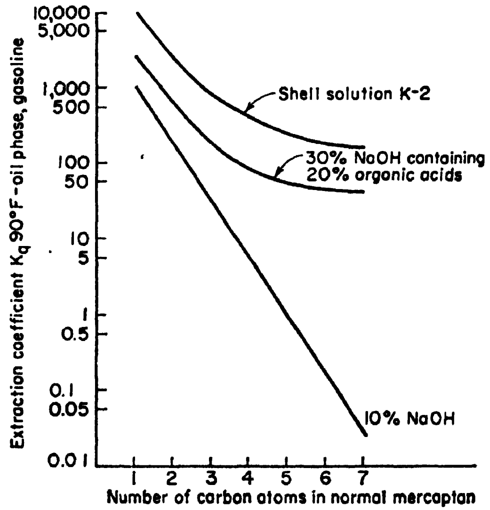

FIG. 14-5. Extraction coefficients (9).

of lower-boiling mercaptans, they are more readily treated than virgin. Comparative results are shown in Table 14-3.

Table 14-3. Typical Mercaptan Extraction Results (9)

Feed stock	Mercaptan distribution, %					
	Methyl	Ethyl	Propyl	Butyl	Amyl	Hexyl +
Virgin	4	6	13	19	18	40
Cracked	19	34	18	15	9	5

	Treating solution			Stripping steam, lb/bbl	Mercaptan S, %	
	Per cent caustic	Per cent org. acids	Circ. rate, per cent of charge		Feed	Product[a]
Virgin	10	0	15	10	0.0265	0.0173
	10	0	15	20	0.0265	0.0172
	30	20	15	10	0.0265	0.0050
	30	20	15	20	0.0265	0.0023
Cracked	10	0	15	10	0.0357	0.0083
	10	0	15	20	0.0357	0.0076
	30	20	15	10	0.0357	0.0020
	30	20	15	20	0.0357	0.0008

[a] Calculated for two theoretical treating stages and three theoretical regeneration stages.

Regeneration

Rich extractant is regenerated by steam stripping to drive off the extracted mercaptans or by converting them to disulfides, which are almost insoluble in the extractant. Either air blowing or electrolysis is employed for the conversion step.

Steam Stripping. As illustrated in Fig. 14-6, ease of stripping is a function of the molecular weight of the mercaptans and the composition of the treating solution. Also, mercaptans are more readily stripped from dilute solutions.

In any stripping operation, the degree of stripping increases with the amount of steam and the number of stripping stages. To a large extent the degree of stripping determines the degree of extraction from the feed stock; a highly stripped extractant is required to produce a low-mercaptan product. For the Shell solutizer process, typical steam requirements are as given in Table 14-4 for various Mid-Continent gasolines (9). These quantities are based on use of six theoretical extraction stages and ten theoretical stripping stages. Reducing the extraction stages from six to

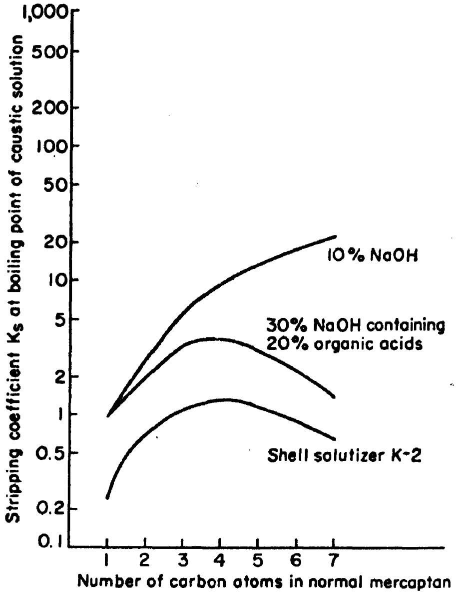

FIG. 14-6. Stripping coefficients (9).

three in the first case would increase stripping-steam requirements by about 50 per cent. The large amounts of steam required to remove the last traces of mercaptans are noteworthy. Because of this large incremental requirement, it is generally not economical to produce a sweet product (4 ppm of mercaptan sulfur) by extraction. Balancing steam requirements against TEL savings, Happel et al., concluded that the optimum product mercaptan level would be about 40 ppm (9).

Table 14-4

Charge stock	RSH sulfur, ppm	Lb of steam/bbl[a]		
		4 ppm	20 ppm	50 ppm
Straight run, 100–260°F	850	25–30	10–15	<5
Straight run, 125–350°F	510	50–65	20–25	10–15
Cracked, 100–400°F	900	20–25	5	<5
Cracked, 230–415°F	640	50–65	20–25	5
Blend, 100–400°F	270	15–20	5	<5

[a] Exclusive of steam to provide sensible heat for heating the circulating solution.

In the Dualayer process, less steam is required (3,19). The "normal" requirement is less than 8 lb per bbl of gasoline treated (7). An eleven-tray column has been used for stripping, and a small amount of light lubricating oil may be added to the stripper feed to prevent foaming.

Sometimes the inventory of extractant is made large enough to permit taking the regeneration system off stream for 8 hr.

Air Blowing. Air regeneration is carried out by blowing the rich extractant with air (CO_2 free) at 125 to 175°F and 40 to 100 psi for 10 to 20 min (27). Air utilization ranges from 15 to 50 per cent of the theoretical. Tannin has been used as an oxidation catalyst (20).

Because disulfides are only slightly soluble in extractant solutions, the bulk of them are separated by settling. Any dissolved or entrained disulfides that are recycled to the extractor are picked up by the feed stock. To avoid this return of sulfur to the feed, the regenerated extractant is often washed with butane, naphtha, or kerosene before it is recycled to the extractor. Good washing results are obtained up to sulfur concentrations of 5 per cent in a naphtha wash (14), up to 4 per cent in a kerosene wash (5).

Electrolytic Regeneration.* Rich extractant is regenerated electrically by forcing the bulk of it past the anode of an electrolytic cell, while forcing a small amount past the cathode. A considerable portion of the mercaptides is converted to disulfides in the cell, either directly (5) or by reaction with oxygen produced at the anode (14,19). Effluent from the anode contains oxygen; it is mixed thoroughly for a sufficient time to complete the regeneration. Effluent from the cathode is first flashed to eliminate hydrogen and is then recycled to the electrolytic cell. As in air regeneration, a hydrocarbon wash is used to remove dissolved or entrained disulfides from the regenerated extractant.

A variation has been proposed, in which sodium ferrocyanide is added to the solution (13). A portion of regenerated extractant is circulated through the electrolyzer to convert ferrocyanide to ferricyanide. Ferricyanide solution is then contacted with rich extractant to oxidize the disulfides, the ferricyanide being reduced to ferrocyanide.

Regenerative Processes

The general features of regenerative mercaptan extraction units are shown in Fig. 14-7. After being caustic washed and coalesced, the feed is contacted countercurrently with the extractant, which picks up mercaptans. Rich extractant is regenerated by steam stripping, air blowing, or electrolysis. In the latter two cases, regenerated extractant is usually washed free of disulfides with a hydrocarbon stream; it is then recycled to the extractor.

Because the various processes employ different extractants (KOH or NaOH) and different solutizing agents, they differ as to process details. In later solutizer units, rotating-disk contactors are used for extraction, and air regeneration is employed (19). The Mercapsol process regener-

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* American Development Corp.

ates by steam stripping, and a small gasoline stripper precedes the mercaptan stripper (19). In the Unisol process, steam stripping is employed, and methanol (solutizing agent) is stripped out with the mercaptans; the stripped methanol is recovered from steam condensate by fractionation. To minimize methanol losses, it is returned to the extractor below the caustic feed. In the Dualayer process, a highly concentrated potassium cresylate solution is used as the extractant, and the extractant is diluted before it is steam stripped to permit any entrained gasoline to separate.

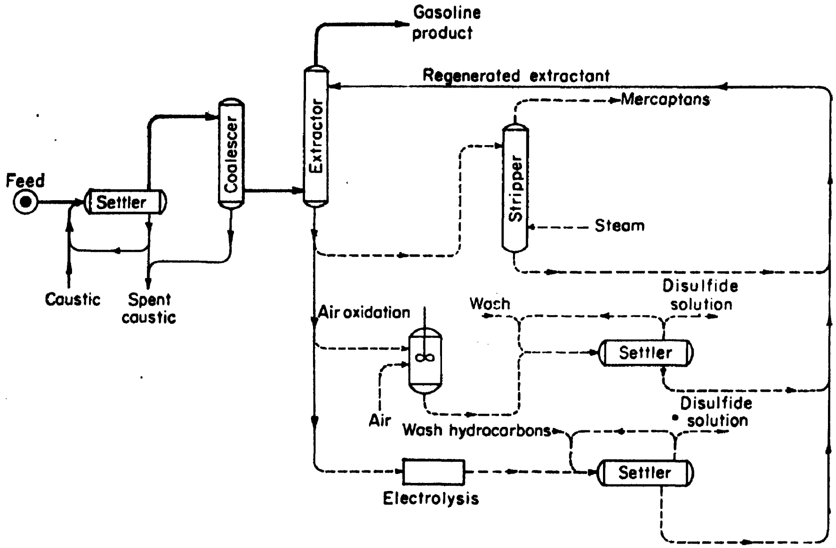

FIG. 14-7. Regenerative mercaptan extraction processes.

Dilution water is removed in the steam-stripping operation to remove mercaptans. Before it is recycled to the extractor, the extractant is contacted (and equilibrated) with a concentrated potassium hydroxide solution (7).

Extractant-circulation requirements for the Dualayer process are usually less than 3 per cent of the feed volume (7). Other processes, which employ less concentrated solvents, require a 10 to 25 per cent treatment (14,27). Operating costs for a 38,000 bbl per day Dualayer plant were quoted at 2.1 cent per bbl in 1957 (7).

Nonregenerative Process

For treating distillate fuels, a nonregenerative Dualayer process is used to improve color, odor, inhibitor response, and oxidation stability (19,25). The process also makes cracked stocks compatible with virgin.

Raw oil is contacted thoroughly at about 130°F with 40 per cent NaOH saturated with cresols. Mercaptans and phenols are extracted from the feed. Effluent is charged to a settler, where three phases form, an upper oil phase, a middle sodium cresylate phase, and a sodium hydroxide phase. Cresylate is discarded, and the caustic is recycled, after being heated to drive off water and restore it to its original concentration.

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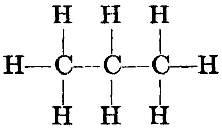
APPENDIX A

NOMENCLATURE OF HYDROCARBONS

As the name implies, hydrocarbons are chemical compounds composed of hydrogen and carbon atoms. Each hydrogen atom has one electron that it shares with another atom; each carbon atom has four such electrons. A chemical linkage is formed between two atoms when each contributes an electron to make a pair that is shared by the two atoms; the pair of shared electrons is called a "bond." Because a hydrogen atom has only one sharable electron, it forms only one bond. With four sharable electrons, a carbon atom forms four bonds. Sometimes two carbon atoms share two pairs of electrons, which constitute a "double bond," or three pairs of electrons, which constitute a "triple bond."

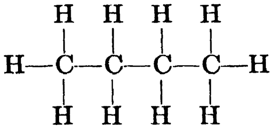
Hydrocarbons are classified according to the manner in which their carbon atoms are linked together. Depending upon their hydrocarbon skeletons, hydrocarbons are classified as paraffins, naphthenes, olefins, diolefins, acetylenes, and aromatics.

Paraffins. Paraffins are hydrocarbons whose carbon atoms form chains, like C—C—C or C—C—C—C, with only single bonds between each pair of carbon atoms. Hydrogen atoms satisfy the remaining linkages of each carbon atom, and the complete molecules are, for example,



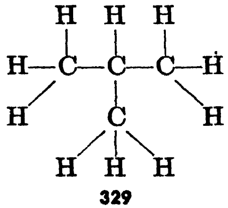
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

or



$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{H} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

If the chain has no branches, the molecule is classified as a normal paraffin (*n*-paraffin). If the chain is branched, the molecule is classified as an *i*-paraffin. The simplest *i*-paraffin contains four carbon atoms. Its carbon skeleton is $\mathrm{C{—}\underset{\underset{\displaystyle C}{|}}{C}{—}C}$, and the complete molecule is



The chemical formulas of all paraffins can be represented by C_nH_{2n+2}, where n is any whole number. Some of the lower-boiling paraffins are listed in Table A-1.

Naphthenes. Naphthenic hydrocarbons are similar to paraffins, except that all or part of the carbon atoms are joined to form a ring. As shown in Table A-2, a naphthenic ring usually contains five or six carbon atoms, although more or fewer are possible. The formation of a ring requires one more carbon-to-carbon bond than does the formation of a chain. Consequently, naphthenes contain less hydrogen than do paraffins. The general formula of single-ring naphthenes is C_nH_{2n}. Chemically, naphthenes are somewhat more reactive than paraffins.

Olefins. An ordinary olefin is similar to a paraffin, except that two of its carbon atoms are connected by a double bond; thus, it has two less hydrogen atoms than the corresponding paraffin, and the general formula is the same as for single-ring naphthenes—C_nH_{2n}. Some lower-boiling olefins are listed in Table A-3.

A cyclic olefin is like a naphthene, although it also has a double bond. The general formula for a single-ring cyclic olefin is C_nH_{2n-2}. Various chemicals add readily to a double bond. Thus, olefins are much more reactive than paraffins or naphthenes, both of which are relatively inert chemically. Their reactivity often makes olefins more valuable than paraffins or naphthenes.

Diolefins. As illustrated in Table A-3, a diolefin contains two double bonds. Diolefins are very reactive chemically and, in high concentrations, are valuable chemicals. When they are present in low concentrations, their high reactivities often make them harmful to product quality, inasmuch as they institute undesirable reactions, such as gum formation in gasoline. The general formula for straight-chain diolefins is C_nH_{2n-2}. For single-ring cyclic diolefins, the general formula is C_nH_{2n-4}.

Acetylenic Hydrocarbons. Acetylenic hydrocarbons are illustrated in Table A-4; they contain triple bonds between two carbon atoms. Like diolefins they are highly reactive, and their reactivity makes them valuable in high concentrations, but usually deleterious in low concentrations. The general formula for acetylenic hydrocarbons is the same as for diolefins, i.e., C_nH_{2n-2} for straight-chain compounds, C_nH_{2n-4} for single-ring cyclic compounds.

Aromatics. Aromatics are compounds that contain at least one six-carbon ring with three double bonds. As illustrated in Table A-6, the rings may be joined together. Aromatics are intermediate in chemical reactivity, and they are often used as chemical building blocks. They are much less reactive, however, than diolefins or acetylenic hydrocarbons, and their chemical reactivity is seldom great enough to constitute a product-quality problem.

Table A-1. Some Paraffinic Hydrocarbons

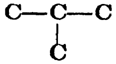
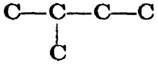
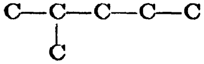
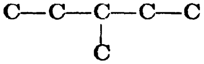
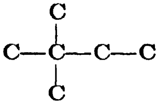
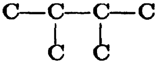
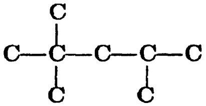
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
1	Methane	C	−259
2	Ethane	C—C	−128
3	Propane	C—C—C	−44
4	*n*-Butane	C—C—C—C	31
5	*n*-Pentane	C—C—C—C—C	97
6	*n*-Hexane	C—C—C—C—C—C	156
7	*n*-Heptane	C—C—C—C—C—C—C	209
8	*n*-Octane	C—C—C—C—C—C—C—C	258
9	*n*-Nonane	C—C—C . . . . C—C	303
10	*n*-Decane	C—C—C . . . . C—C	345
11	*n*-Undecane	C—C—C . . . . C—C	385
12	*n*-Dodecane	C—C—C . . . . C—C	421
16	Cetane	C—C—C . . . . C—C	547
4	*i*-Butane	 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C}$	11
5	*i*-Pentane	 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C-C}$	82
6	2-Methylpentane	 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C-C-C}$	141
6	3-Methylpentane	 $\mathrm{C-C-\underset{\underset{C}{\vert}}{C}-C-C}$	146
6	Neohexane	 $\mathrm{C-\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}-C-C}$	122
6	Diisopropyl	 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-\underset{\underset{C}{\vert}}{C}-C}$	136
8	*i*-Octane	 $\mathrm{C-\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}-C-\underset{\underset{C}{\vert}}{C}-C}$	211

Table A-2. Some Naphthenic Hydrocarbons

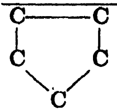
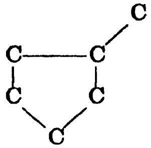
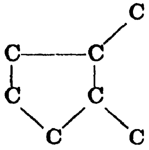
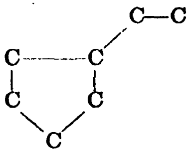
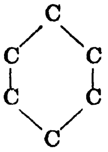
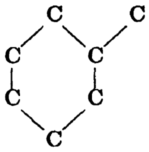
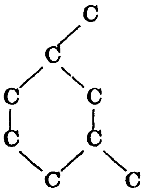
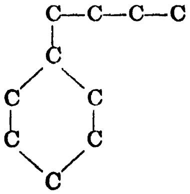
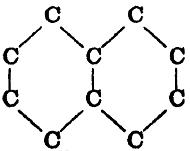
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
5	Cyclopentane		121
6	Methylcyclopentane		161
7	1,2-Dimethylcyclopentane		
7	Ethylcyclopentane		218
6	Cyclohexane		177
7	Methylcyclohexane		214
8	1-3-Dimethylcyclohexane		254
10	*n*-Butylcyclohexane		
10	Decalin		373

Table A-3. Some Olefinic Hydrocarbons

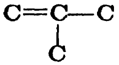
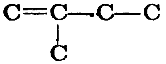
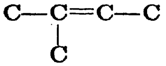
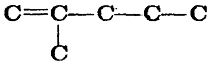
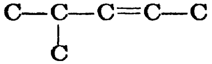
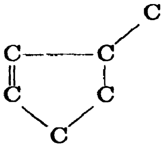
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
2	Ethylene	C=C	−155
3	Propene	C=C—C	−54
4	*n*-Butene-1	C=C—C—C	21
4	*n*-Butene-2	C—C=C—C	36
5	*n*-Pentene-1	C=C—C—C—C	86
5	*n*-Pentene-2	C—C=C—C—C	98
6	*n*-Hexene-1	C=C—C—C—C—C	146
6	*n*-Hexene-3	C—C—C=C—C—C	154
4	*i*-Butene	 $\mathrm{C{=}\underset{\substack{\vert\\ C}}{C}{-}C}$	20
5	*i*-Pentene-1	 $\mathrm{C{=}\underset{\substack{\vert\\ C}}{C}{-}C{-}C}$	88
5	*i*-Pentene-2	 $\mathrm{C{-}\underset{\substack{\vert\\ C}}{C}{=}C{-}C}$	101
6	2-Methylpentene-1	 $\mathrm{C{=}\underset{\substack{\vert\\ C}}{C}{-}C{-}C{-}C}$	144
6	2-Methylpentene-3	 $\mathrm{C{-}\underset{\substack{\vert\\ C}}{C}{-}C{=}C{-}C}$	134
6	Methylcyclopentene		

Table A-4. Some Diolefinic Hydrocarbons

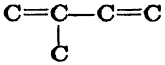
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
4	Butadiene	C=C—C=C	24
5	Pentadiene-1,3	C=C—C=C—C	100
5	Pentadiene-1,4	C=C—C—C=C	
5	Isoprene	 $\mathrm{C{=}\underset{\substack{\vert\\ C}}{C}{-}C{=}C}$	98

Table A-5. Some Acetylenic Hydrocarbons

Carbon atoms	Name	Carbon skeleton	Boiling point, °F
2	Acetylene	C≡C	
3	Propine	C≡C—C	−10
4	Butine-1	C≡C—C—C	47
4	Butine-2	C—C≡C—C	81

Table A-6. Some Aromatic Hydrocarbons

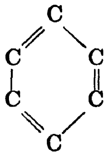
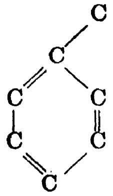
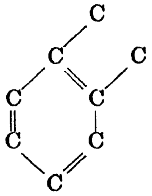
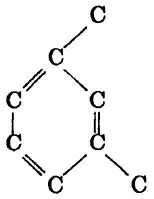
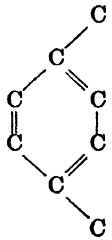
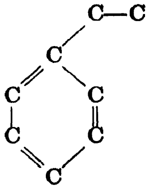
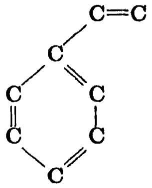
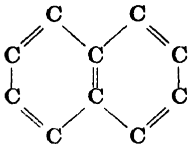
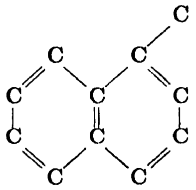
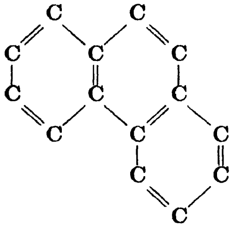
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
6	Benzene		176
7	Toluene		231
8	*o*-Xylene		292
8	*m*-Xylene		282
8	*p*-Xylene		281

Table A-6. Some Aromatic Hydrocarbons (Continued)

Carbon atoms	Name	Carbon skeleton	Boiling point, °F
8	Ethylbenzene		277
8	Styrene		293
10	Naphthalene		424
11	1-Methylnaphthalene		467
14	Phenanthrene		644

APPENDIX B

DEGREES API AND SPECIFIC GRAVITIES

The density of a hydrocarbon is usually expressed in terms of °API. The relationships among °API at 60°F, specific gravity (60°F/60°F), and pounds per U.S. gallon at 60°F are as follows:

°API	Sp. gr.	Lb/gal
0	1.076	8.96
5	1.037	8.63
10	1.000	8.33
15	0.966	8.04
20	0.934	7.78
25	0.904	7.53
30	0.876	7.30
35	0.850	7.08
40	0.825	6.87
45	0.802	6.68
50	0.780	6.49
55	0.759	6.32
60	0.739	6.15
65	0.720	5.99
70	0.702	5.85
75	0.685	5.70
80	0.669	5.57
85	0.654	5.44
90	0.639	5.32
95	0.625	5.20
100	0.611	5.09

INDEX