4 Introduction to Refining Processes

4.1 INTRODUCTION

In the crude state, petroleum has minimal value, but when refined, it provides high-value liquid fuels, solvents, lubricants, and many other products (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2011a,b, 2014). The fuels derived from petroleum contribute approximately one-third to one-half of the total world energy supply and are used not only for transportation fuels (i.e., gasoline, diesel fuel, and aviation fuel, among others) but also to heat buildings. Petroleum products have a wide variety of uses that vary from gaseous and liquid fuels to near-solid machinery lubricants. In addition, the residue of many refinery processes, asphalt—a once-maligned by-product—is now a premium value product for highway surfaces, roofing materials, and miscellaneous waterproofing uses.

In a very general sense, petroleum refining can be traced back over 5000 years to the times when asphalt materials and oils were isolated from areas where natural seepage occurred (Abraham, 1945; Forbes, 1958; Hoiberg, 1960). Any treatment of the asphalt (such as hardening in the air prior to use) or of the oil (such as allowing for more volatile components to escape prior to use in lamps) may be considered to be refining under the general definition of refining. However, petroleum refining as we know it is a very recent science and many innovations evolved during the twentieth century.

Briefly, petroleum refining is the separation of petroleum into fractions and the subsequent treating of these fractions to yield marketable products (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2011a,b, 2014). In fact, a refinery is essentially a group of manufacturing plants that vary in number with the variety of products produced (Figure 4.1). Refinery processes must be selected and products are manufactured to give a balanced operation in which petroleum is converted into a variety of products in amounts that are in accord with the demand for each. For example, the manufacture of products from the lower-boiling portion of petroleum automatically produces a certain amount of higher-boiling components. If the latter cannot be sold as, say, heavy fuel oil, these products will accumulate until refinery storage facilities are full. To prevent the occurrence of such a situation, the refinery must be flexible and be able to change operations as needed. This usually means more processes: thermal processes to change an excess of heavy fuel oil into more gasoline with coke as the residual product, or a vacuum distillation process to separate the heavy oil into lubricating oil blend stocks and asphalt.

As the basic elements of crude oil, hydrogen and carbon form the main input into a refinery, combining into thousands of individual constituents, and the economic recovery of these constituents varies with the individual petroleum according to its particular individual qualities and the processing facilities of a particular refinery. In general, crude oil, once refined, yields three basic groupings of products that are produced when it is broken down into cuts or fractions (Table 4.1). The gas and gasoline cuts form the lower-boiling products and are usually more valuable than the higher-boiling fractions and provide gas (liquefied petroleum gas), naphtha, aviation fuel, motor fuel, and feedstocks for the petrochemical industry (Table 4.2). Naphtha, a precursor to gasoline and solvents, is produced from the light and middle range of distillate cuts (sometimes referred to collectively as light gas oil) and is also used as a feedstock for the petrochemical industry (Table 4.3). The middle distillates refer to products from the middle boiling range of petroleum and include kerosene, diesel

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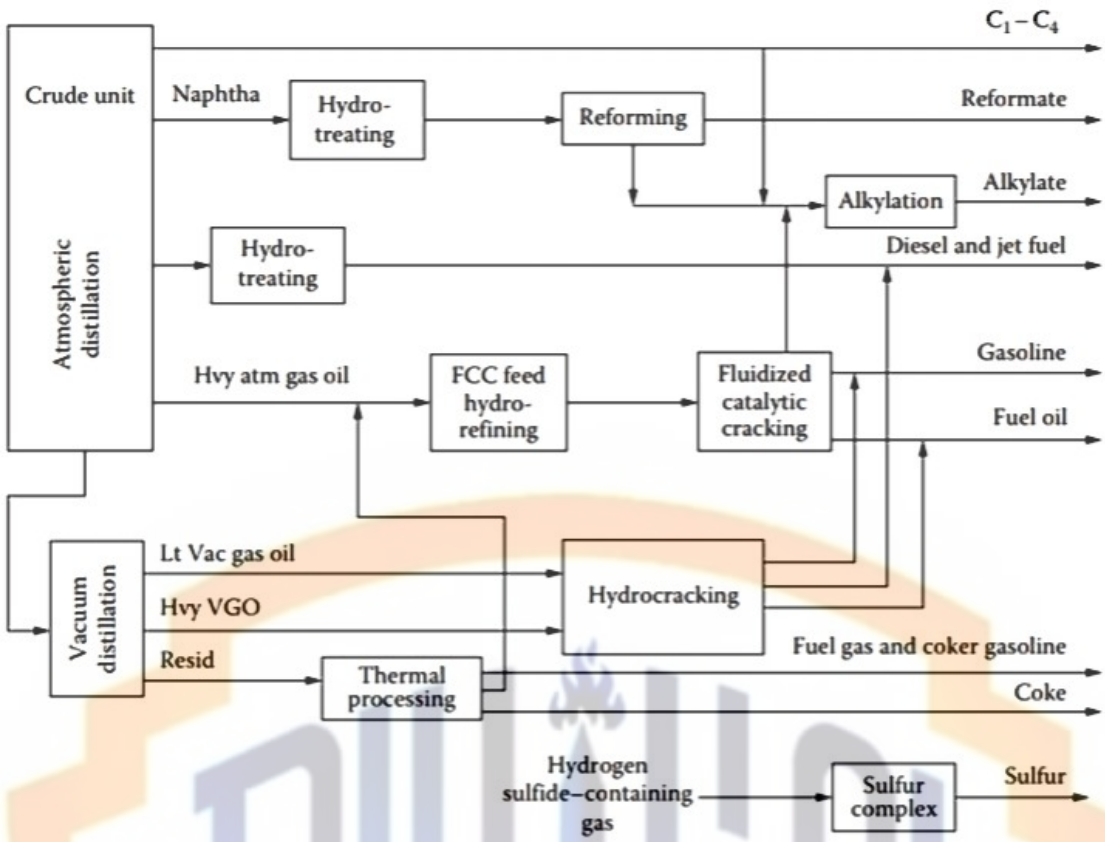

FIGURE 4.1 Schematic overview of a refinery.

TABLE 4.1
Boiling Fractions of Crude Petroleum

Fraction	Boiling Range[a] (°C)	(°F)
Light naphtha	−1–150	30–300
Gasoline	−1–180	30–355
Heavy naphtha	150–205	300–400
Kerosene	205–260	400–500
Light gas oil	260–315	400–600
Heavy gas oil	315–425	600–800
Lubricating oil	>400	>750
Vacuum gas oil	425–600	800–1100
Residuum	>510	>950

[a] For convenience, boiling ranges are converted to the nearest 5°.

fuel, distillate fuel oil, and light gas oil. Waxy distillate and lower-boiling lubricating oils are sometimes included in the middle distillates. The remainder of the crude oil includes the higher-boiling lubricating oils, gas oil, and residuum (the nonvolatile fraction of the crude oil). The residuum can also produce heavy lubricating oils and waxes but is more often sued for asphalt production. The complexity of petroleum is emphasized insofar as the actual proportions of light, medium, and heavy fractions vary significantly from one crude oil to another.

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TABLE 4.2
Production of Starting Materials for Petrochemical Processing

Starting Feedstock	Process	Product
Petroleum	Distillation	Light ends
		Methane
		Ethane
		Propane
		Butane
	Catalytic cracking	Ethylene
		Propylene
		Butylenes
		Higher olefins
	Coking	Ethylene
		Propylene
		Butylenes
		Higher olefins
Natural gas	Refining/gas processing	Methane
		Ethane
		Propane
		Butane

TABLE 4.3
Sources of Naphtha

Process	Primary Product	Secondary Process	Secondary Product
Atmospheric distillation	Light naphtha	Cracking	Petrochemical feedstocks
	Heavy naphtha	Catalytic cracking	Light naphtha
	Gas oil	Catalytic cracking	Light naphtha
	Gas oil	Hydrocracking	Light naphtha
Vacuum distillation	Gas oil	Catalytic cracking	Light naphtha
		Hydrocracking	Light naphtha
	Residuum	Coking	Light naphtha
		Hydrocracking	Light naphtha

The refining industry has been the subject of the four major forces that affect most industries and that have hastened the development of new petroleum refining processes: (1) the demand for products such as gasoline, diesel, fuel oil, and jet fuel; (2) feedstock supply, specifically the changing quality of crude oil and geopolitics between different countries and the emergence of alternate feed supplies such as bitumen from tar sand, natural gas, and coal; (3) environmental regulations that include more stringent regulations in relation to sulfur in gasoline and diesel; and (4) technology development such as new catalysts and processes.

In the early days of the twentieth century, refining processes were developed to extract kerosene for lamps. Any other products were considered to be unusable and were usually discarded. Thus, the first refining processes were developed to purify, stabilize, and improve the quality of kerosene. However, the invention of the internal combustion engine led (at approximately the time of World War I) to a demand for gasoline for use in increasing quantities as a motor fuel for cars and trucks.

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This demand on the lower-boiling products increased, particularly when the market for aviation fuel developed. Thereafter, refining methods had to be constantly adapted and improved to meet the quality requirements and needs of car and aircraft engines.

Since then, the general trend throughout refining has been to produce more products from each barrel of petroleum and to process those products in different ways to meet the product specifications for use in modern engines. Overall, the demand for gasoline has rapidly expanded, and demand has also developed for gas oils and fuels for domestic central heating and fuel oil for power generation, as well as for light distillates and other inputs, derived from crude oil, for the petrochemical industries.

As the need for the lower-boiling products developed, petroleum yielding the desired quantities of the lower-boiling products became less available, and refineries had to introduce conversion processes to produce greater quantities of lighter products from the higher-boiling fractions. The means by which a refinery operates in terms of producing the relevant products depends not only on the nature of the petroleum feedstock but also on its configuration (i.e., the number of types of the processes that are employed to produce the desired product slate), and the refinery configuration is, therefore, influenced by the specific demands of a market. Therefore, refineries need to be constantly adapted and upgraded to remain viable and responsive to ever-changing patterns of crude supply and product market demands. As a result, refineries have been introducing increasingly complex and expensive processes to gain higher yields of lower-boiling products from the higher-boiling fractions and residua.

To convert crude oil into desired products in an economically feasible and environmentally acceptable manner, refinery processes for crude oil are generally divided into three categories: (1) separation processes, of which distillation is the prime example; (2) conversion processes, of which coking and catalytic cracking are prime example; and (3) finishing processes, of which hydrotreating to remove sulfur is a prime example.

The simplest refinery configuration is the *topping refinery*, which is designed to prepare feedstocks for petrochemical manufacture or for the production of industrial fuels. The topping refinery consists of tankage, a distillation unit, recovery facilities for gases and light hydrocarbons, and the necessary utility systems (steam, power, and water-treatment plants). Topping refineries produce large quantities of unfinished oils and are highly dependent on local markets, but the addition of hydrotreating and reforming units to this basic configuration results in a more flexible *hydroskimming refinery*, which can also produce desulfurized distillate fuels and high-octane gasoline. These refineries may produce up to half of their output as residual fuel oil, and they face increasing market loss as the demand for low-sulfur (even no-sulfur) high-sulfur fuel oil increases.

The most versatile refinery configuration is the *conversion refinery*. A conversion refinery incorporates all the basic units found in both the topping and hydroskimming refineries, but it also features gas oil conversion plants such as catalytic cracking and hydrocracking units, olefin conversion plants such as alkylation or polymerization units, and, frequently, coking units for sharply reducing or eliminating the production of residual fuels. Modern conversion refineries may produce two-thirds of their output as unleaded gasoline, with the balance distributed between liquefied petroleum gas, jet fuel, diesel fuel, and a small quantity of coke. Many such refineries also incorporate solvent extraction processes for manufacturing lubricants and petrochemical units with which to recover propylene, benzene, toluene, and xylenes for further processing into polymers.

Finally, the yields and quality of refined petroleum products produced by any given oil refinery depend on the mixture of crude oil used as feedstock and the configuration of the refinery facilities. Light/sweet crude oil is generally more expensive and has inherent great yields of higher-value low-boiling products such as naphtha, gasoline, jet fuel, kerosene, and diesel fuel. Heavy sour crude oil is generally less expensive and produces greater yields of lower-value higher-boiling products that must be converted into lower-boiling products (Speight, 2013, 2014).

Since a refinery is a group of integrated manufacturing plants (Figure 4.1) that are selected to give a balanced production of saleable products in amounts that are in accord with the demand for

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each, it is necessary to prevent the accumulation of nonsaleable products, and the refinery must be flexible and be able to change operations as needed. The complexity of petroleum is emphasized insofar as the actual amounts of the products vary significantly from one crude oil to another (Speight, 2014, 2016). In addition, the configuration of refineries may vary from refinery to refinery. Some refineries may be more oriented toward the production of gasoline (large reforming and/or catalytic cracking), whereas the configuration of other refineries may be more oriented toward the production of middle distillates such as jet fuel and gas oil.

This chapter presents an introduction to petroleum refining in order for the reader to place each process in the correct context of the refinery.

4.2 DEWATERING AND DESALTING

Petroleum is recovered from the reservoir mixed with a variety of substances: gases, water, and dirt (minerals). Thus, refining actually commences with the production of fluids from the well or reservoir and is followed by pretreatment operations that are applied to the crude oil either at the refinery or prior to transportation. Pipeline operators, for instance, are insistent upon the quality of the fluids put into the pipelines; therefore, any crude oil to be shipped by pipeline or, for that matter, by any other form of transportation must meet rigid specifications in regard to water and salt content. In some instances, sulfur content, nitrogen content, and viscosity may also be specified. Field separation, which occurs at a field site near the recovery operation, is the first attempt to remove the gases, water, and dirt that accompany crude oil coming from the ground. The separator may be no more than a large vessel that gives a quieting zone for gravity separation into three phases: gases, crude oil, and water containing entrained dirt.

Thus, the first step in petroleum processing, even before the crude oil enters the refinery, occurs at the wellhead (Abdel-Aal et al., 2016). It is at this stage that fluids from the well are separated into crude oil, natural gas, and water phases using a gas–oil separator. The separators can be horizontal, vertical, or spherical and are generally classified into two types based on the number of phases to separate: (1) two-phase separators, which are used to separate gas from oil in oil fields or gas from water for gas fields, and (2) three-phase separators, which are used to separate the gas from the liquid phase and water from oil. The liquid (oil, emulsion) leaves at the bottom through a level control or an exit valve. The gas leaves the vessel at the top, passing through a mist extractor to remove the small liquid droplets in the gas. Separators can also be categorized according to their operating pressure: (1) low-pressure units can tolerate pressures on the order of 10–180 psi, (2) medium-pressure separators operate from 230 to 700 psi, and (3) high-pressure units can tolerate pressures of 975–1500 psi. Even after this type of separation and before separation of petroleum into its various constituents can proceed, there is the need to clean the petroleum. This is often referred to as desalting and dewatering in which the goal is to remove water and the constituents of the brine that accompany the crude oil from the reservoir to the wellhead during recovery operations.

Desalting is a water-washing operation performed at the production field and at the refinery site for additional crude oil cleanup (Figure 4.2). If the petroleum from the separators contains water and dirt, water washing can remove much of the water-soluble minerals and entrained solids. If these crude oil contaminants are not removed, they can cause operating problems during refinery processing, such as equipment plugging and corrosion as well as catalyst deactivation.

The usual practice is to blend crude oils of similar characteristics, although fluctuations in the properties of the individual crude oils may cause significant variations in the properties of the blend over a period of time. Blending several crude oils prior to refining can eliminate the frequent need to change the processing conditions that may be required to process each of the crude oils individually.

However, simplification of the refining procedure is not always the end result. Incompatibility of different crude oils, which can occur if, for example, a paraffinic crude oil is blended with heavy asphaltic oil, can cause sediment formation in the unrefined feedstock or in the products, thereby complicating the refinery process.

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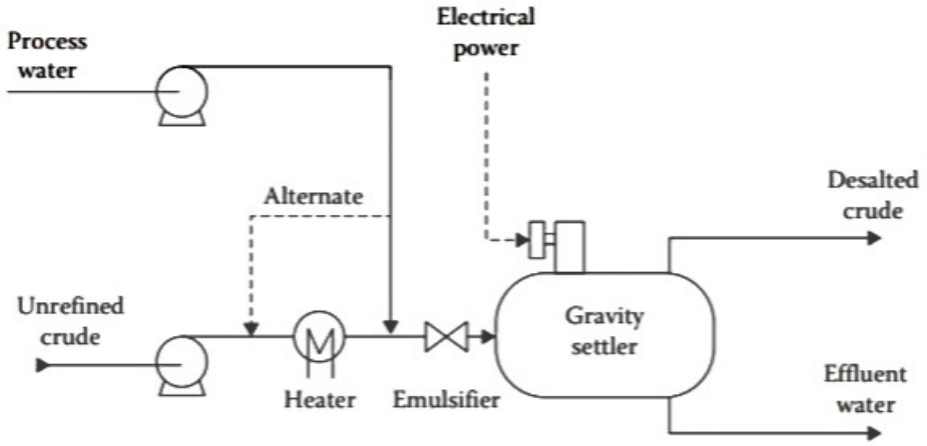

FIGURE 4.2 An electrostatic desalting unit. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

4.3 DISTILLATION

In the early stages of refinery development, when illuminating and lubricating oils were the main products, distillation was the major, and often only, refinery process. At that time, gasoline was a minor product but, as the demand for gasoline increased, conversion processes were developed, because distillation could no longer supply the necessary quantities.

It is possible to obtain products ranging from gaseous materials taken off at the top of the distillation column to a nonvolatile residue or reduced crude (*bottoms*), with correspondingly lighter materials at intermediate points. The reduced crude may then be processed by vacuum, or steam, distillation in order to separate the high-boiling lubricating oil fractions without the danger of decomposition, which occurs at high (>350°C, >660°F) temperatures. Atmospheric distillation may be terminated with a lower-boiling fraction (*cut*) if it is felt that vacuum or steam distillation will yield a better-quality product or if the process appears to be economically more favorable. Not all crude oils yield the same distillation products (Table 4.1)—although there may be variations by several degrees in the boiling ranges of the fractions as specified by different companies—and the nature of the crude oil dictates the processes that may be required for refining.

Distillation was the first method by which petroleum was refined. The original technique involved a batch operation in which the still was a cast-iron vessel mounted on brickwork over a fire and the volatile materials were passed through a pipe or gooseneck that led from the top of the still to a condenser. The latter was a coil of pipe (*worm*) immersed in a tank of running water.

Heating a batch of crude petroleum caused the more volatile, lower-boiling components to vaporize and then condense in the worm to form naphtha. As the distillation progressed, the higher-boiling components became vaporized and were condensed to produce kerosene: the major petroleum product of the time. When all of the possible kerosene had been obtained, the material remaining in the still was discarded. The still was then refilled with petroleum and the operation repeated.

The capacity of the stills at that time was usually several barrels of petroleum and if often required 3 or more days to distill (*run*) a batch of crude oil. The simple distillation as practiced in the 1860s and 1870s was notoriously inefficient. The kerosene was more often than not contaminated by naphtha, which distilled during the early stages, or by heavy oil, which distilled from the residue during the final stages of the process. The naphtha generally rendered the kerosene so flammable explosions accompanied that ignition. On the other hand, the presence of heavier oil adversely affected the excellent burning properties of the kerosene and created a great deal of smoke. This condition could be corrected by redistilling (*rerunning*) the kerosene, during which process the more volatile fraction (*front end*) was recovered as additional naphtha, while the kerosene residue (*tail*) remaining in the still was discarded.

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The 1880s saw the introduction of the continuous distillation of petroleum. The method employed a number of stills coupled together in a row, and each still was heated separately and was hotter than the preceding one. The stills were arranged so that oil flowed by gravity from the first to the last. Crude petroleum in the first still was heated so that a light naphtha fraction distilled from it before the crude petroleum flowed into the second still, where a higher temperature caused the distillation of a heavier naphtha fraction. The residue then flowed to the third still where an even higher temperature caused kerosene to distill. The oil thus progressed through the battery to the last still, where destructive distillation (thermal decomposition; cracking) was carried out to produce more kerosene. The residue from the last still was removed continuously for processing into lubricating oils or for use as fuel oil.

In the early 1900s, a method of partial (or selective) condensation was developed to allow a more exact separation of petroleum fractions. A partial condenser was inserted between the still and the conventional water-cooled condenser. The lower section of the tower was packed with stones and insulated with brick so that the heavier less volatile material entering the tower condensed and drained back into the still. Noncondensed material passed into another section where more of the less volatile material was condensed on air-cooled tubes, and the condensate was withdrawn as a petroleum fraction. The noncondensable (overhead) material from the air-cooled section entered a second tower that also contained air-cooled tubes and often produced a second fraction. The volatile material remaining at this stage was then condensed in a water-cooled condenser to yield a third fraction. The van Dyke tower is essentially one of the first stages in a series of improvements that ultimately led to the distillation units found in modern refineries, which separate petroleum fractions by fractional distillation.

4.3.1 Distillation at Atmospheric Pressure

The present-day petroleum distillation unit is, like the battery of the 1800s, a collection of distillation units but, in contrast to the early battery units, a tower is used in the typical modern refinery (Figure 4.3) and brings about a fairly efficient degree of fractionation (separation).

The feed to a distillation tower is heated by flow through pipes arranged within a large furnace. The heating unit is known as a pipe still heater or pipe still furnace, and the heating unit and the fractional distillation tower make up the essential parts of a distillation unit or pipe still. The pipe still furnace heats the feed to a predetermined temperature—usually a temperature at which a predetermined portion of the feed will change into vapor. The vapor is held under pressure in the pipe in the furnace until it discharges as a foaming stream into the fractional distillation tower. The unvaporized or liquid portion of the feed descends to the bottom of the tower to be pumped away as a bottom nonvolatile product, while the vaporized material passes up the tower to be fractionated into gas oils, kerosene, and naphtha.

Pipe still furnaces vary greatly and, in contrast to the early units where capacity was usually 200–500 bbl per day, can accommodate 25,000 bbl or more of crude petroleum per day. The walls and ceiling are insulated with firebrick, and the interior of the furnace is partially divided into two sections: a smaller convection section where the oil first enters the furnace and a larger section (fitted with heaters) and where the oil reaches its highest temperature.

Another twentieth-century innovation in distillation is the use of heat exchangers that are also used to preheat the feed to the furnace. These exchangers are bundles of tubes arranged within a shell so that a feedstock passes through the tubes in the opposite direction a heated feedstock passing through the shell. By this means, cold crude oil is passed through a series of heat exchangers where hot products from the distillation tower are cooled before entering the furnace and as a heated feedstock. This results in a saving of heater fuel and is a major factor in the economical operation of modern distillation units.

All of the primary fractions from a distillation unit are equilibrium mixtures and contain some of the lower-boiling constituents that are characteristic of a lower-boiling fraction. The primary fractions are *stripped* of these constituents (*stabilized*) before storage or further processing.

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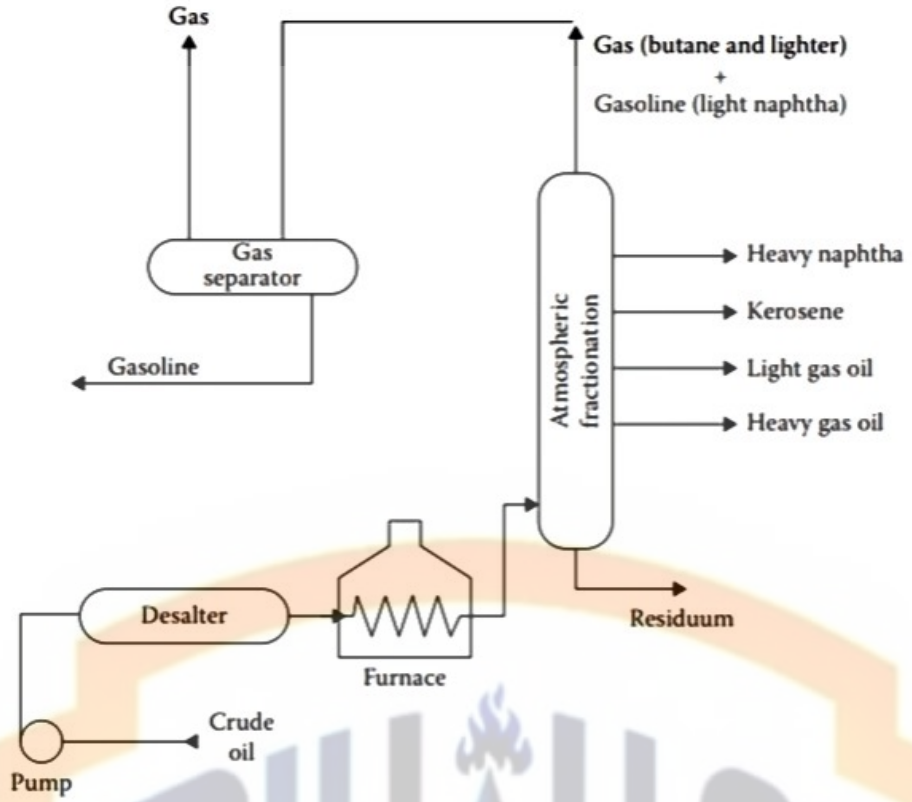

FIGURE 4.3 An atmospheric distillation unit. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

4.3.2 Distillation under Reduced Pressure

Distillation under reduced pressure (vacuum distillation) as applied to the petroleum refining industry is truly a technique of the twentieth century and has since wide use in petroleum refining. Vacuum distillation evolved because of the need to separate the less volatile products, such as lubricating oils, from the petroleum without subjecting these high-boiling products to cracking conditions. The boiling point of the heaviest cut obtainable at atmospheric pressure is limited by the temperature (ca. 350°C; ca. 660°F) at which the residue starts to decompose (*crack*). When the feedstock is required for the manufacture of lubricating oils, further fractionation without cracking is desirable and this can be achieved by distillation under vacuum conditions.

Operating conditions for vacuum distillation (Figure 4.4) are usually 50–100 mm of mercury (atmospheric pressure = 760 mm of mercury). In order to minimize large fluctuations in pressure in the vacuum tower, the units are necessarily of a larger diameter than the atmospheric units. Some vacuum distillation units have diameters on the order of 45 ft (14 m). By this means, a heavy gas oil may be obtained as an overhead product at temperatures of approximately 150°C (300°F), and lubricating oil cuts may be obtained at temperatures of 250°C–350°C (480°F–660°F), feed and residue temperatures being kept below the temperature of 350°C (660°F), above which cracking will occur. The partial pressure of the hydrocarbons is effectively reduced still further by the injection of steam. The steam added to the column, principally for the stripping of asphalt in the base of the column, is superheated in the convection section of the heater.

The fractions obtained by vacuum distillation of the reduced crude (atmospheric residuum) from an atmospheric distillation unit depend on whether or not the unit is designed to produce lubricating or vacuum gas oils. In the former case, the fractions include (1) heavy gas oil, which is an overhead product and is used as catalytic cracking stock or, after suitable treatment, a light lubricating oil; (2) lubricating oil (usually three fractions—light, intermediate, and heavy), which

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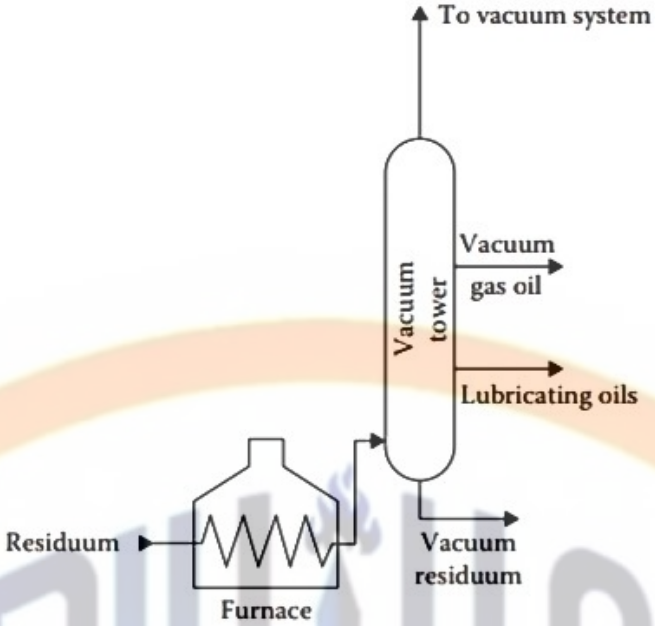

FIGURE 4.4 A vacuum distillation unit. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

is obtained as a sidestream product; and (3) asphalt (or residuum), which is the bottom product and may be used directly as, or to produce, asphalt and which may also be blended with gas oils to produce a heavy fuel oil.

In the early refineries, distillation was the prime means by which products were separated from crude petroleum. As the technologies for refining evolved into the twenty-first century, refineries became much more complex (Figure 4.1), but distillation remained the prime means by which petroleum is refined. Indeed, the distillation section of a modern refinery (Figures 4.3 and 4.4) is the most flexible section in the refinery since conditions can be adjusted to process a wide range of refinery feedstocks from the lighter crude oils to the heavier more viscous crude oils. However, the maximum permissible temperature (in the vaporizing furnace or heater) to which the feedstock can be subjected is 350°C (660°F). Thermal decomposition occurs above this temperature that, if it occurs within a distillation unit, can lead to coke deposition in the heater pipes or in the tower itself with the resulting failure of the unit.

The contained use of atmospheric and vacuum distillation has been a major part of refinery operations during this century, and no doubt will continue to be employed throughout the remainder of the century as the primary refining operation.

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4.4 THERMAL PROCESSES

Cracking was used commercially in the production of oils from coal and shales before the petroleum industry began, and the discovery that the heavier products could be decomposed to lighter oils was used to increase the production of kerosene and was called cracking distillation.

The precise origins of cracking distillation are unknown. It is rumored that, in 1861, the attending stillman had to leave his charge for a longer time than he intended (the reason is not known) during which time the still overheated. When he returned he noticed that the distillate in the collector was much more volatile than anticipated at that particular stage of the distillation. Further investigation led to the development of cracking distillation (i.e., thermal degradation with the simultaneous production of distillate).

Cracking distillation (thermal decomposition with simultaneous removal of distillate) was recognized as a means of producing the valuable lighter product (kerosene) from heavier nonvolatile materials. In the early days of the process (1870–1900) the technique was very simple—a batch of crude oil was heated until most of the kerosene had been distilled from it and the overhead material had become dark in color. At this point, distillation was discontinued and the heavy oils were held in the hot zone, during which time some of the high-molecular-weight components were decomposed to produce lower-molecular-weight products. After a suitable time, distillation was continued to yield light oil (kerosene) instead of the heavy oil that would otherwise have been produced.

The yields of kerosene products were usually markedly increased by means of cracking distillation, but the technique was not suitable for gasoline production. As the need for gasoline arose in the early 1900s, the necessity of prolonging the cracking process became apparent and a process known as pressure cracking evolved.

Pressure cracking was a batch operation in which, as an example, gas oil (200 bbl) was heated to approximately 425°C (800°F) in stills that had been reinforced to operate at pressures as high as 95 psi. The gas oil was held under maximum pressure for 24 hours, while fires maintained the temperature. Distillation was then started and during the next 48 hours produces a lighter distillate (100 bbl) that contained the gasoline components. This distillate was treated with sulfuric acid to remove unstable gum-forming components and then redistilled to produce a cracked gasoline (boiling range).

The large-scale production of cracked gasoline was first developed by Burton in 1912. The process employed batch distillation in horizontal shell stills and operated at approximately 400°C (ca. 750°F) and 75–95 psi. It was the first successful method of converting heavier oils into gasoline. Nevertheless, heating a bulk volume of oil was soon considered cumbersome, and during the years 1914–1922, a number of successful continuous cracking processes were developed. By these processes, gas oil was continuously pumped through a unit that heated the gas oil to the required temperature, held it for a time under pressure, and then discharged the cracked material into distillation equipment where it was separated into gases, gasoline, gas oil, and tar.

The tube-and-tank cracking process is not only typical of the early (post-1900) cracking units but also is one of the first units on record in which the concept of reactors (soakers) being onstream/offstream is realized. Such a concept departs from the true batch concept and allowed a greater

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degree of continuity. In fact, the tube-and-tank cracking unit may be looked upon as a forerunner of the delayed coking operation.

In the tube-and-tank process, a feedstock (at that time a gas oil) was preheated by exchange with the hot products from the unit pumped into the cracking coil, which consisted of several hundred feet of very strong pipe that lined the inner walls of a furnace where oil or gas burners raised the temperature of the gas oil to 425°C (800°F). The hot gas oil passed from the cracking coil into a large reaction chamber (soaker) where the gas oil was held under the temperature and pressure conditions long enough for the cracking reactions to be completed. The cracking reactions formed coke that, in the course of several days, filled the soaker. The gas oil stream was then switched to a second soaker, and the first soaker was cleaned out by drilling operations similar to those used in drilling an oil well.

The cracked material (other than coke) left the onstream soaker to enter an evaporator (tar separator) maintained under a much lower pressure than the soaker where, because of the lower pressure, all of the cracked material, except the tar, became vaporized. The vapor left the top of the separator where it was distilled into separate fractions—gases, gasoline, and gas oil. The tar that was deposited in the separator was pumped out for use as asphalt or as a heavy fuel oil.

Early in the development of tube-and-tank thermal cracking, it was found that adequate yields of gasoline could not be obtained by one passage of the stock through the heating coil; attempts to increase the conversion in one pass brought about undesirable high yields of gas and coke. It was better to crack to a limited extent, remove the products, and recycle the rest of the oil (or a distilled fraction free of tar) for repeated partial conversion. The high-boiling constituents once exposed to cracking were so changed in composition as to be more refractory than the original feedstock.

With the onset of the development of the automobile, the most important part of any refinery became the gasoline-manufacturing facilities. Among the processes that have evolved for gasoline production are thermal cracking, catalytic cracking, thermal reforming, catalytic reforming, polymerization, alkylation, coking, and distillation of fractions directly from crude petroleum.

When kerosene was the major product, gasoline was the portion of crude petroleum too volatile to be included in kerosene. The refiners of the 1890s and early 1900s had no use for it and often dumped an accumulation of gasoline into the creek or river that was usually nearby. As the demand for gasoline increased with the onset of World War I and the ensuing 1920s, more crude oil had to be distilled not only to meet the demand for gasoline but also to reduce the overproduction of the heavier petroleum fractions, including kerosene.

The problem of how to produce more gasoline from less crude oil was solved in 1913 by the incorporation of cracking units into refinery operations in which fractions heavier than gasoline were converted into gasoline by thermal decomposition. The early (pre-1940) processes employed for gasoline manufacture were processes in which the major variables involved were feedstock type, time, temperature, and pressure, which need to be considered to achieve the cracking of the feedstock to lighter products with minimal coke formation.

As refining technology evolved throughout this century, the feedstocks for cracking processes became the residuum or heavy distillate from a distillation unit. In addition, the residual oils produced as the end products of distillation processes and even some of the heavier virgin oils often contain substantial amounts of asphaltic materials, which preclude the use of the residuum as fuel oils or lubricating stocks. However, subjecting these residua directly to thermal processes has become economically advantageous, since, on the one hand, the end result is the production of lower-boiling salable materials; on the other hand, the asphaltic materials in the residua are regarded as the unwanted coke-forming constituents.

As the thermal processes evolved and catalysts were employed with more frequency, poisoning of the catalyst with a concurrent reduction in the lifetime of the catalyst became a major issue for refiners. To avoid catalyst poisoning, it became essential that as much of the nitrogen and metals (such as vanadium and nickel) as possible should be removed from the feedstock. The majority of the heteroatoms (nitrogen, oxygen, and sulfur) and the metals are contained in, or associated

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4.4.1 Thermal Cracking

One of the earliest conversion processes used in the petroleum industry is the thermal decomposition of higher-boiling materials into lower-boiling products. This process is known as thermal cracking, and the exact origins of the process are unknown. The process was developed in the early 1900s to produce gasoline from the "unwanted" higher-boiling products of the distillation process. However, it was soon learned that the thermal cracking process also produced a wide slate of products varying from highly volatile gases to nonvolatile coke.

The heavier oils produced by cracking are light and heavy gas oils as well as a residual oil that could also be used as heavy fuel oil. Gas oils from catalytic cracking were suitable for domestic and industrial fuel oils or as diesel fuels when blended with straight-run gas oils. The gas oils produced by cracking were also a further important source of gasoline. In a once-through cracking operation, all of the cracked material is separated into products and may be used as such. However, the gas oils produced by cracking (cracked gas oils) are more resistant to cracking (more refractory) than gas oils produced by distillation (straight-run gas oils) but could still be cracked to produce more gasoline. This was achieved using a later innovation (post-1940) involving a recycle operation in which the cracked gas oil was combined with fresh feed for another trip through the cracking unit. The extent to which recycling was carried out affected the yield of gasoline from the process.

The majority of the thermal cracking processes use temperatures of 455°C–540°C (850°F–1005°F) and pressures of 100–1000 psi; the Dubbs process may be taken as a typical application of an early thermal cracking operation. The feedstock (reduced crude) is preheated by direct exchange with the cracking products in the fractionating columns. Cracked gasoline and heating oil are removed from the upper section of the column. Light and heavy distillate fractions are removed from the lower section and are pumped to separate heaters. Higher temperatures are used to crack the more refractory light distillate fraction. The streams from the heaters are combined and sent to a soaking chamber where additional time is provided to complete the cracking reactions. The cracked products are then separated in a low-pressure flash chamber where a heavy fuel oil is removed as bottoms. The remaining cracked products are sent to the fractionating columns.

Mild cracking conditions, with a low conversion per cycle, favor a high yield of gasoline components, with low gas and coke production, but the gasoline quality is not high, whereas more severe conditions give increased gas and coke production and reduced gasoline yield (but of higher quality). With limited conversion per cycle, the heavier residues must be recycled, but these recycle oils become increasingly refractory upon repeated cracking, and if they are not required as a fuel oil stock they may be coked to increase gasoline yield or refined by means of a hydrogen process.

The thermal cracking of higher-boiling petroleum fractions to produce gasoline is now virtually obsolete. The antiknock requirements of modern automobile engines together with the different

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nature of crude oils (compared to those of 50 or more years ago) have reduced the ability of the thermal cracking process to produce gasoline on an economic basis. Very few new units have been installed since the 1960s, and some refineries may still operate the older cracking units.

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4.5 CATALYTIC PROCESSES

There are many processes in a refinery that employ a catalyst to improve process efficiency (Table 4.5). The original incentive arose from the need to increase gasoline supplies in the 1930s and 1940s. Since cracking could virtually double the volume of gasoline from a barrel of crude oil, cracking was justifiable on this basis alone.

In the 1930s, thermal cracking units produced approximately 50% of the total gasoline. The octane number of this gasoline was approximately 70 compared to approximately 60 for straight-run (distilled) gasoline. The thermal reforming and polymerization processes that were developed during the 1930s could be expected to further increase the octane number of gasoline to some extent, but an additional innovation was needed to increase the octane number of gasoline to enhance the development of more powerful automobile engines.

4.5.1 Catalytic Cracking

In 1936, a new cracking process opened the way to higher-octane gasoline—this process was catalytic cracking. This process is basically the same as thermal cracking but differs by the use of a catalyst, which is not (in theory) consumed in the process, and directs the course of the cracking reactions to produce more of the desired higher-octane hydrocarbon products.

Catalytic cracking has a number of advantages over thermal cracking: (1) the gasoline produced has a higher octane number; (2) the catalytically cracked gasoline consists largely of *iso*-paraffins

TABLE 4.5
Summary of Catalytic Cracking Processes

Conditions
Solid acidic catalyst (such as silica–alumina and zeolite).
Temperature: 480°C–540°C (900°F–1000°F (solid/vapor contact).
Pressure: 10–20 psi.
Provisions needed for continuous catalyst replacement with heavier feedstocks (residua).
Catalyst may be regenerated or replaced.
Feedstocks
Gas oils and residua
Residua pretreated to remove salts (metals)
Residua pretreated to remove high molecular weight (asphaltic constituents)
Products
Lower molecular weight than feedstock
Some gases (feedstock and process parameters dependent)
Iso-paraffins in product
Coke deposited on catalyst
Variations
Fixed bed
Moving bed
Fluidized bed

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and aromatics, which have high octane numbers and greater chemical stability than monoolefins and diolefins that are present in much greater quantities in thermally cracked gasoline. Substantial quantities of olefinic gases suitable for polymer gasoline manufacture and smaller quantities of methane, ethane, and ethylene are produced by catalytic cracking. Sulfur compounds are changed in such a way that the sulfur content of catalytically cracked gasoline is lower than in thermally cracked gasoline. Catalytic cracking produces less heavy residual or tar and more of the useful gas oils than does thermal cracking. The process has considerable flexibility, permitting the manufacture of both motor and aviation gasoline and a variation in the gas oil yield to meet changes in the fuel oil market.

The last 40 years have seen substantial advances in the development of catalytic processes. This has involved not only rapid advances in the chemistry and physics of the catalysts themselves but also major engineering advances in reactor design. For example, the evolution of the design of the catalyst beds from fixed beds to moving beds to fluidized beds. Catalyst chemistry/physics and bed design have allowed major improvements in process efficiency and product yields.

Catalytic cracking is another innovation that truly belongs to the twentieth century and is regarded as the modern method for converting high-boiling petroleum fractions, such as gas oil, into gasoline and other low-boiling fractions. Thus, catalytic cracking in the usual commercial process involves contacting a gas oil fraction with an active catalyst under suitable conditions of temperature, pressure, and residence time so that a substantial part (>50%) of the gas oil is converted into gasoline and lower-boiling products, usually in a single-pass operation.

However, during the cracking reaction, carbonaceous material is deposited on the catalyst, which markedly reduces its activity, and removal of the deposit is very necessary. This is usually accomplished by burning the catalyst in the presence of air until catalyst activity is reestablished.

The several processes currently employed in catalytic cracking differ mainly in the method of catalyst handling, although there is overlap with regard to catalyst type and the nature of the products.

The catalyst, which may be an activated natural or synthetic material, is employed in bead, pellet, or microspherical form and can be used as a fixed bed, moving bed, or fluid bed. The fixed-bed process was the first process to be used commercially and uses a static bed of catalyst in several reactors, which allows a continuous flow of feedstock to be maintained. Thus, the cycle of operations consists of (1) flow of feedstock through the catalyst bed, (2) discontinuance of feedstock flow and removal of coke from the catalyst by burning, and (3) insertion of the reactor onstream. The moving-bed process uses a reaction vessel (in which cracking takes place) and a kiln (in which the spent catalyst is regenerated) and catalyst movement between the vessels is provided by various means.

The *fluid-bed catalytic cracking process* (Figure 4.9) differs from the fixed-bed and moving-bed processes, insofar as the powdered catalyst is circulated essentially as a fluid with the feedstock. The several fluid catalytic cracking processes in use differ primarily in mechanical design. Side-by-side reactor–regenerator construction along with unitary vessel construction (the reactor either above or below the regenerator) is the two main mechanical variations.

4.5.2 Catalysts

Natural clays have long been known to exert a catalytic influence on the cracking of oils, but it was not until about 1936 that the process using silica–alumina catalysts was developed sufficiently for commercial use. Since then, catalytic cracking has progressively supplanted thermal cracking as the most advantageous means of converting distillate oils into gasoline. The main reason for the wide adoption of catalytic cracking is the fact that a better yield of higher-octane gasoline can be obtained than by any known thermal operation. At the same time, the gas

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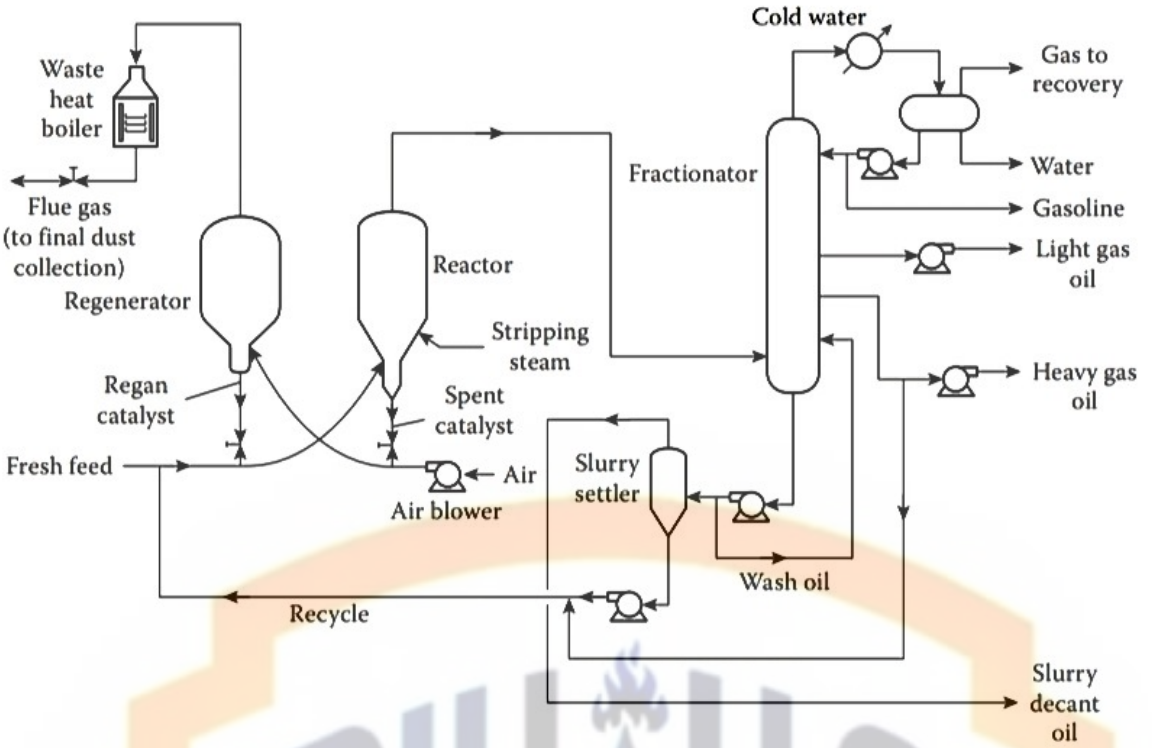

FIGURE 4.9 A fluid catalytic cracking unit.

produced consists mostly of propane and butane with less methane and ethane. The production of heavy oils and tars, higher in molecular weight than the charge material, is also minimized, and both the gasoline and the uncracked "cycle oil" are more saturated than the products of thermal cracking.

The major innovations of the twentieth century lie not only in reactor configuration and efficiency but also in catalyst development. There is probably not an oil company in the United States that does not have some research and development activity related to catalyst development. Much of the work is proprietary and, therefore, can only be addressed here in generalities.

The cracking of crude oil fractions occurs over many types of catalytic materials, but high yields of desirable products are obtained with hydrated aluminum silicates. These may be either activated (acid-treated) natural clays of the bentonite type of synthesized silica–alumina or silica–magnesia preparations. Their activity to yield essentially the same products may be enhanced to some extent by the incorporation of small amounts of other materials such as the oxides of zirconium, boron (which has a tendency to volatilize away on use), and thorium. Natural and synthetic catalysts can be used as pellets or beads and also in the form of powder; in either case, replacements are necessary because of attrition and gradual loss of efficiency. It is essential that they be stable to withstand the physical impact of loading and thermal shocks and that they withstand the action of carbon dioxide, air, nitrogen compounds, and steam. They also should be resistant to sulfur and nitrogen compounds and synthetic catalysts, or certain selected clays, appear to be better in this regard than average untreated natural catalysts.

The catalysts are porous and highly adsorptive, and their performance is affected markedly by the method of preparation. Two chemically identical catalysts having pores of different size and distribution may have different activity, selectivity, temperature coefficients of reaction rates, and responses to poisons. The intrinsic chemistry and catalytic action of a surface may be independent of pore size, but small pores produce different effects because of the manner in which hydrocarbon vapors are transported into and out of the pore systems.

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produced in this manner.

4.7 REFORMING PROCESSES

When the demand for higher-octane gasoline developed during the early 1930s, attention was directed to ways and means of improving the octane number of fractions within the boiling range of gasoline. Straight-run (distilled) gasoline frequently had very low octane numbers, and any process that would improve the octane numbers would aid in meeting the demand for gasoline with higher octane number. Such a process (called thermal reforming) was developed and used widely, but to a much lesser extent than thermal cracking. Thermal reforming was a natural development from older thermal cracking processes; cracking converts heavier oils into gasoline whereas reforming converts (reforms) gasoline into higher-octane gasoline. The equipment for thermal reforming is essentially the same as for thermal cracking, but higher temperatures are used.

4.7.1 Thermal Reforming

In carrying out thermal reforming, a feedstock such as 205°C (400°F) end-point naphtha or a straight-run gasoline is heated to 510°C–595°C (950°F–1100°F) in a furnace, much the same as a cracking furnace, with pressures from 400 to 1000 psi. As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The material then enters a fractional distillation tower where any heavy products are separated. The remainder of the reformed material leaves the top of the tower to be separated into gases and reformate. The higher octane number of the reformate is due primarily to the cracking of longer-chain paraffins into higher-octane olefins.

The products of thermal reforming are gases, gasoline, and residual oil or tar, the latter being formed in very small amounts (approximately 1%). The amount and quality of the gasoline, known as reformate, are very dependent on the temperature. A general rule is the higher the reforming temperature, the higher the octane number, but the lower the yield of reformate.

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Thermal reforming is less effective and less economical than catalytic processes and has been largely supplanted. As it used to be practiced, a single-pass operation was employed at temperatures in the range of 540°C–760°C (1000°F–1140°F) and pressures of approximately 500–1000 psi. The degree of improvement of the octane number depended on the extent of conversion but was not directly proportional to the extent of crack per pass. However, at very high conversions, the production of coke and gas became prohibitively high. The gases produced were generally olefinic, and the process required either a separate gas polymerization operation or one in which C_3–C_4 gases were added back to the reforming system.

More recent modifications of the thermal reforming process due to the inclusion of hydrocarbon gases with the feedstock are known as gas reversion and polyforming. Thus, olefinic gases produced by cracking and reforming can be converted into liquids boiling in the gasoline range by heating them under high pressure. Since the resulting liquids (polymers) have high octane numbers, they increase the overall quantity and quality of gasoline produced in a refinery.

4.7.2 Catalytic Reforming

The catalytic reforming process was commercially nonexistent in the United States prior to 1940. The process is really a process of the 1950s and showed phenomenal growth in 1953–1959 time period.

Like thermal reforming, catalytic reforming converts low-octane gasoline into high-octane gasoline (reformate). When thermal reforming could produce reformate with research octane numbers of 65–80 depending on the yield, catalytic reforming produces reformate with octane numbers on the order of 90–95. Catalytic reforming is conducted in the presence of hydrogen over hydrogenation–dehydrogenation catalysts, which may be supported on alumina or silica–alumina. Depending on the catalyst, a definite sequence of reactions takes place, involving structural changes in the feedstock. This more modern concept actually rendered thermal reforming somewhat obsolescent.

The commercial processes available for use can be broadly classified as the moving-bed, fluid-bed, and fixed-bed types. The fluid-bed and moving-bed processes used mixed nonprecious metal oxide catalysts in units equipped with separate regeneration facilities. Fixed-bed processes use predominantly platinum-containing catalysts in units equipped for cycle, occasional, or no regeneration.

Catalytic reformer feeds are saturated (i.e., not olefinic) materials; in the majority of cases that feed may be a straight-run naphtha but other by-product low-octane naphtha (e.g., coker naphtha) can be processed after treatment to remove olefins and other contaminants. Hydrocracker naphtha that contains substantial quantities of naphthenes is also a suitable feed.

Dehydrogenation is a main chemical reaction in catalytic reforming, and hydrogen gas is consequently produced in large quantities. The hydrogen is recycled through the reactors where the reforming takes place to provide the atmosphere necessary for the chemical reactions and also prevents the carbon from being deposited on the catalyst, thus extending its operating life. An excess of hydrogen above whatever is consumed in the process is produced, and, as a result, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a by-product.

Catalytic reforming is usually carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace where the mixture is heated to the desired temperature, 450°C–520°C (840°F–965°F) and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100–1000 psi (Figure 4.12). Normally, pairs of reactors are used in series with heaters located between adjoining reactors in order to compensate for the endothermic reactions taking place. Sometimes, as many as four or five reactors are kept onstream in series, while one or more is being regenerated.

The onstream cycle of any one reactor may vary from several hours to many days, depending on the feedstock and reaction conditions.

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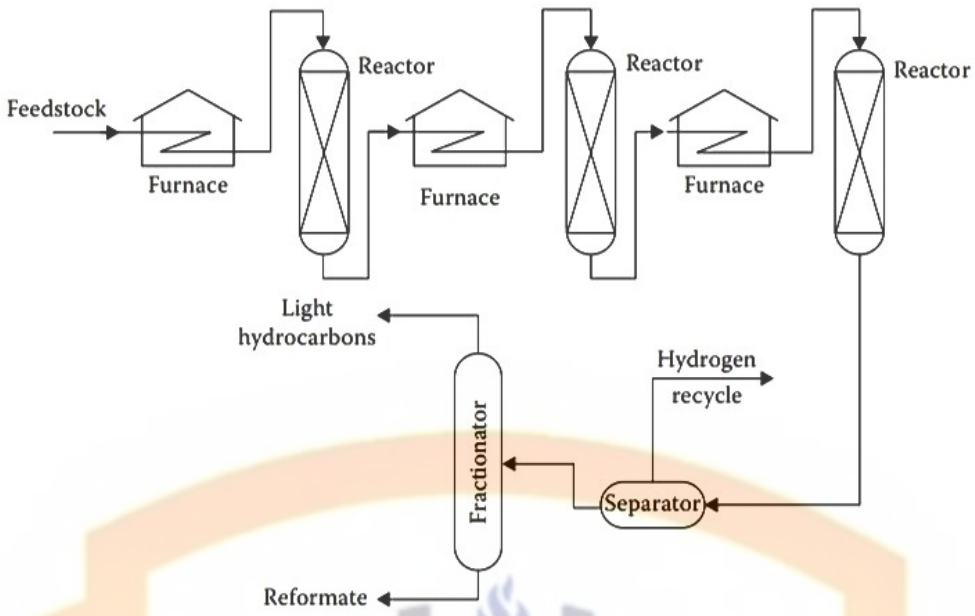

FIGURE 4.12 Catalytic reforming. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

4.7.3 Catalysts

The composition of a reforming catalyst is dictated by the composition of the feedstock and the desired reformate. The catalysts used are principally molybdena–alumina, chromia–alumina, or platinum on a silica–alumina or alumina base. The nonplatinum catalysts are widely used in regenerative process for feeds containing, for example, sulfur, which poisons platinum catalysts, although pretreatment processes (e.g., hydrodesulfurization) may permit platinum catalysts to be employed.

The purpose of platinum on the catalyst is to promote dehydrogenation and hydrogenation reactions, that is, the production of aromatics, participation in hydrocracking, and rapid hydrogenation of carbon-forming precursors. For the catalyst to have an activity for the isomerization of both paraffins and naphthenes—the initial cracking step of hydrocracking—and to participate in paraffin dehydrocyclization, it must have an acid activity. The balance between these two activities is most important in a reforming catalyst. In fact, in the production of aromatics from cyclic saturated materials (naphthenes), it is important that hydrocracking be minimized to avoid loss of the desired product and, thus, the catalytic activity must be moderated relative to the case of gasoline production from a paraffinic feed, where dehydrocyclization and hydrocracking play an important part.

4.8 ISOMERIZATION PROCESSES

Catalytic reforming processes provide high-octane constituents in the heavier gasoline fraction, but the normal paraffin components of the lighter gasoline fraction, especially butanes, pentanes, and hexanes, have poor octane ratings. The conversion of these normal paraffins to their isomers (isomerization) yields gasoline components of high octane rating in this lower-boiling range. Conversion is obtained in the presence of a catalyst (aluminum chloride activated with hydrochloric acid), and it is essential to inhibit side reactions such as cracking and olefin formation.

Isomerization—another innovation of the twentieth century—found initial commercial applications during World War II for making high-octane aviation gasoline components and additional

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feed for alkylation units. The lowered alkylate demands in the post-World War II period led to the majority of the butane isomerization units being shut down. In recent years, the greater demand for high-octane motor fuel has resulted in new butane isomerization units being installed.

4.8.1 Processes

The earliest process of note was the production of *iso*-butane, which is required as an alkylation feed. The isomerization may take place in the vapor phase, with the activated catalyst supported on a solid phase, or in the liquid phase with a dissolved catalyst. In the process, pure butane or a mixture of isomeric butanes (Figure 4.13) is mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 110°C–170°C (230°F–340°F) and 200–300 psi. The product is cooled, the hydrogen separated, and the cracked gases are then removed in a stabilizer column. The stabilizer bottom product is passed to a superfractionator where the normal butane is separated from the *iso*-butane.

Present isomerization applications in petroleum refining are used with the objective of providing additional feedstock for alkylation units or high-octane fractions for gasoline blending (Table 4.7). Straight-chain paraffins (*n*-butane, *n*-pentane, *n*-hexane) are converted to respective *iso*-compounds by continuous catalytic (aluminum chloride, noble metals) processes. Natural gasoline or light straight-run gasoline can provide feed by first fractionating as a preparatory step. High volumetric yields (>95%) and 40%–60% conversion per pass are characteristic of the isomerization reaction.

4.8.2 Catalysts

During World War II, aluminum chloride was the catalyst used to isomerize butane, pentane, and hexane. Since then, supported metal catalysts have been developed for use in high-temperature processes that operate in the range of 370°C–480°C (700°F–900°F) and 300–750 psi, while aluminum chloride plus hydrogen chloride are universally used for the low-temperature processes.

Nonregenerable aluminum chloride catalyst is employed with various carriers in a fixed-bed or liquid contactor. Platinum or other metal catalyst processes utilized fixed-bed operation and can

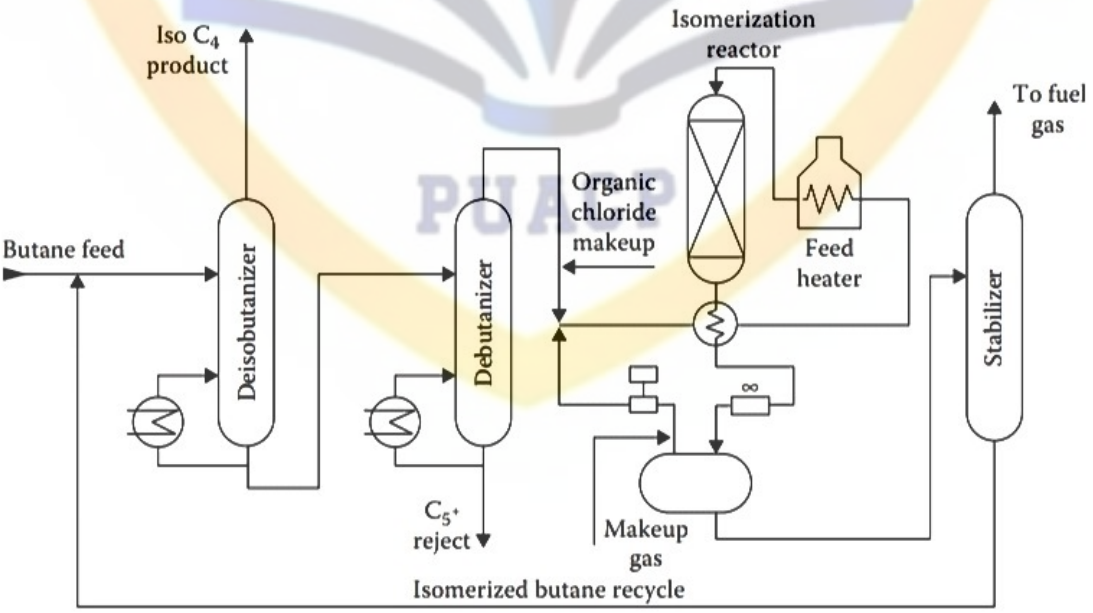

FIGURE 4.13 A butane isomerization unit. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

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TABLE 4.7
Component Streams for Gasoline

Stream	Producing Process	Boiling Range (°C)	Boiling Range (°F)
Paraffinic			
Butane	Distillation Conversion	0	32
Iso-pentane	Distillation Conversion Isomerization	27	81
Alkylate	Alkylation	40–150	105–300
Isomerate	Isomerization	40–70	105–160
Naphtha	Distillation	30–100	85–212
Hydrocrackate	Hydrocracking	40–200	105–390
Olefinic			
Catalytic naphtha	Catalytic cracking	40–200	105–390
Cracked naphtha	Steam cracking	40–200	105–390
Polymer	Polymerization	60–200	140–390
Aromatic			
Catalytic reformate	Catalytic reforming	40–200	105–390

be regenerable or nonregenerable. The reaction conditions vary widely depending on the particular process and feedstock: 40°C–480°C (100°F–900°F) and 150–1000 psi.

4.9 ALKYLATION PROCESSES

The combination of olefins with paraffins to form higher *iso*-paraffins is termed *alkylation*. Since olefins are reactive (unstable) and are responsible for exhaust pollutants, their conversion to high-octane *iso*-paraffins is desirable when possible. In refinery practice, only *iso*-butane is alkylated by reaction with *iso*-butene or normal butene and *iso*-octane is the product. Although alkylation is possible without catalysts, commercial processes use aluminum chloride, sulfuric acid, or hydrogen fluoride as catalysts, when the reactions can take place at low temperatures, minimizing undesirable side reactions, such as polymerization of olefins.

Alkylate is composed of a mixture of *iso*-paraffins that have octane numbers that vary with the olefins from which they were made. Butylenes produce the highest octane numbers, propylene the lowest, and pentylene derivatives the intermediate values. All alkylates, however, have high octane numbers (>87) that make them particularly valuable. The alkylation process is another twentieth-century refinery innovation and developments in petroleum processing in the late 1930s and during World War II was directed toward the production of high-octane liquids for aviation gasoline. The sulfuric acid process was introduced in 1938, and hydrogen fluoride alkylation was introduced in 1942. Rapid commercialization took place during the war to supply military needs, but many of these plants were shut down at the end of the war.

In the mid-1950s, aviation gasoline demand started to decline, but motor gasoline quality requirements rose sharply. Wherever practical, refiners shifted the use of alkylate to premium motor fuel. To aid in the improvement of the economics of the alkylation process and also the sensitivity of the premium gasoline pool, additional olefins were gradually added to alkylation feed. New plants were built to alkylate propylene and the butylenes (butanes) produced in the refinery rather than the butane–butylene stream formerly used.

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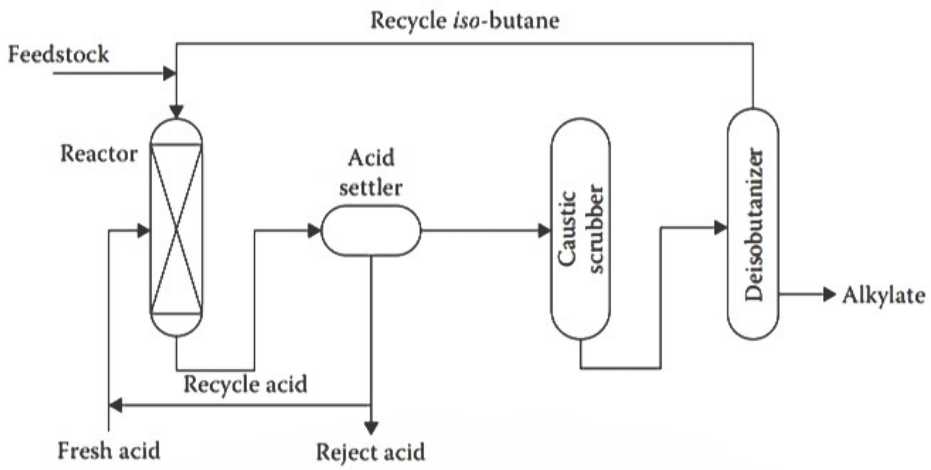

FIGURE 4.14 An alkylation unit (sulfuric acid catalyst). (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

4.9.1 Processes

The alkylation reaction as now practiced in petroleum refining is the union, through the agency of a catalyst, of an olefin (ethylene, propylene, butylene, and amylene) with *iso*-butane to yield high-octane branched-chain hydrocarbons in the gasoline boiling range. Olefin feedstock is derived from the gas produced in a catalytic cracker, while *iso*-butane is recovered by refinery gases or produced by catalytic butane isomerization.

To accomplish this, either ethylene or propylene is combined with *iso*-butane at 50°C–280°C (125°F–450°F) and 300–1000 psi in the presence of metal halide catalysts such as aluminum chloride. Conditions are less stringent in catalytic alkylation; olefins (propylene, butylene derivatives, or pentylene derivatives) are combined with *iso*-butane in the presence of an acid catalyst (sulfuric acid or hydrofluoric acid) at low temperatures and pressures (1°C–40°C, 30°F–105°F, and 14.8–150 psi) (Figure 4.14).

4.9.2 Catalysts

Sulfuric acid, hydrogen fluoride, and aluminum chloride are the general catalysts used commercially. Sulfuric acid is used with propylene and higher-boiling feeds, but not with ethylene, because it reacts to form ethyl hydrogen sulfate. The acid is pumped through the reactor and forms an air emulsion with reactants, and the emulsion is maintained at 50% acid. The rate of deactivation varies with the feed and *iso*-butane charge rate. Butene feeds cause less acid consumption than the propylene feeds.

Aluminum chloride is not widely used as an alkylation catalyst but when employed, hydrogen chloride is used as a promoter and water is injected to activate the catalyst as an aluminum chloride/hydrocarbon complex. Hydrogen fluoride is used for the alkylation of higher-boiling olefins, and the advantage of hydrogen fluoride is that it is more readily separated and recovered from the resulting product.

4.10 POLYMERIZATION PROCESSES

In the petroleum industry, polymerization is the process by which olefin gases are converted to liquid products that may be suitable for gasoline (polymer gasoline) or other liquid fuels. The feedstock usually consists of propylene and butylenes from cracking processes or may even be selective olefins for dimer, trimer, or tetramer production.

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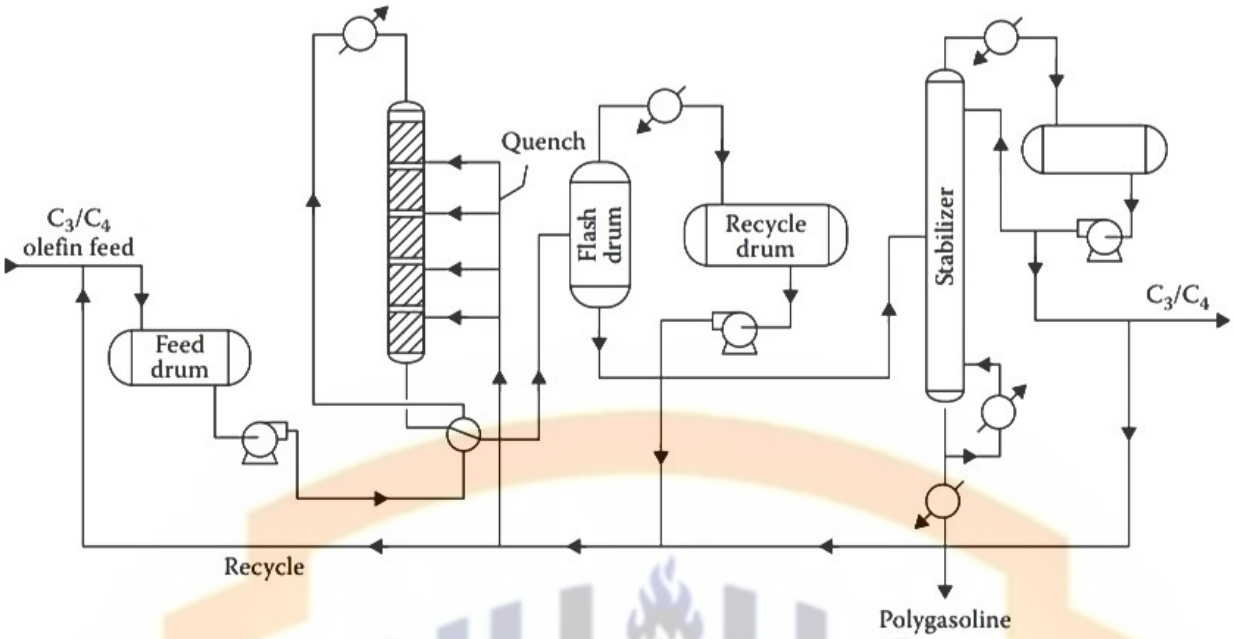

FIGURE 4.15 A polymerization unit. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum refining processes, 1999, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.)

Polymerization is a process that can claim to be the earliest process to employ catalysts on a commercial scale. Catalytic polymerization came into use in the 1930s and was one of the first catalytic processes to be used in the petroleum industry.

4.10.1 Processes

Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures. Thermal polymerization is regarded as not being as effective as catalytic polymerization but has the advantage that it can be used to "polymerize" saturated materials that cannot be induced to react by catalysts. The process consists of vapor-phase cracking of, for example, propane and butane followed by prolonged periods at the high temperature (510°C–595°C, 950°F–1100°F) for the reactions to proceed to near completion.

Olefins can also be conveniently polymerized by means of an acid catalyst (Figure 4.15). Thus, the treated, olefin-rich feed stream is contacted with a catalyst (sulfuric acid, copper pyrophosphate, phosphoric acid) at 150°C–220°C (300°F–425°F) and 150–1200 psi, depending on feedstock and product requirement.

4.10.2 Catalysts

Phosphates are the principal catalysts used in polymerization units; the commercially used catalysts are liquid phosphoric acid, phosphoric acid on kieselguhr, copper pyrophosphate pellets, and phosphoric acid film on quartz. The latter is the least active, but the most used and easiest one to regenerate simply by washing and recoating; the serious disadvantage is that tar must occasionally be burned off the support. The process using liquid phosphoric acid catalyst is far more responsible to attempts to raise production by increasing temperature than the other processes.

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4.6 OCTANE NUMBER

This is an important test for measuring the antiknock quality of the gasoline (petrol or motor spirit). The knocking of the motor fuels is compared using blends of reference fuels. The standard reference fuels used for octane numbers below 100 are iso-octane and normal heptane which are assigned values of 100 and 0, respectively, on the octane number scale. The octane number of the fuel is defined as the volume percentage of iso-octane (2, 2, 4-trimethyl pentane) in a blend with n-heptane which is equal to the test fuel in knock intensity under standardised and closely controlled conditions of test in a single-cylinder, variable compression ratio engines, known as CFR engines. Thus, a fuel of 87 octane number has a CFR engine performance matching that obtainable with a blend of 87 volume percent iso-octane and 13 volume percent n-heptane. The rating can be done by either Research method or Motor method. The differences in the two methods are as follows:

	Research method	*Motor method*
rpm	600	900
Spark advance	13° btdc	Variable
Mixture heating	No	Yes

Octane number requirements of gasoline engines depend on their compression ratio. If the fuel meets the minimum requirements in respect of octane number it ensures trouble free operation. Apart from being a nuisance, the knocking in an engine may result in loss of energy and at times may cause severe damage to the engine.

4.7 PERFORMANCE NUMBER

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