



## Petroleum refining



Oil refinery near Donaldsonville, Louisiana, U.S.

*Keith Wood—Stone/Getty Images*

**petroleum refining**, conversion of crude oil into useful products.

### HISTORY

### DISTILLATION OF KEROSENE AND NAPHTHA

The refining of crude petroleum owes its origin to the successful drilling of the first oil well in Titusville,

Pennsylvania, U.S., in 1859. Prior to that time, petroleum was available only in very small quantities from natural seepage of subsurface oil in various areas throughout the world. However, such limited availability restricted the uses for petroleum to medicinal and specialty purposes. With the discovery of "rock oil" in northwestern Pennsylvania, crude oil became available in sufficient quantity to inspire the development of larger-scale processing systems. The earliest refineries employed simple distillation units, or "stills," to separate the various constituents of petroleum by heating the crude oil mixture in a vessel and condensing the resultant vapours into liquid fractions. Initially the primary product was kerosene, which proved to be a more abundant, cleaner-burning lamp oil of more consistent quality than whale oil or animal fat.

The lowest-boiling raw product from the still was "straight run" naphtha, a forerunner of unfinished gasoline (petrol). Its initial commercial application was primarily as a solvent. Higher-boiling materials were found to be effective as lubricants and fuel oils, but they were largely novelties at first.

The perfection of oil-drilling techniques quickly spread to Russia, and by 1890 refineries there were producing large quantities of kerosene and fuel oils. The development of the internal-combustion engine in the later years of the 19th century created a small market for crude naphtha. But the development of the automobile at the turn of the century sharply increased the demand for quality gasoline, and this finally provided a home for the petroleum fractions that were too volatile to be included in kerosene. As demand for automotive fuel rose, methods for continuous distillation of crude oil were developed.

### CONVERSION TO LIGHT FUELS

After 1910 the demand for automotive fuel began to outstrip the market requirements for kerosene, and refiners were pressed to develop new technologies to increase gasoline yields. The earliest process, called thermal cracking, consisted of heating heavier oils (for which there was a

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low market requirement) in pressurized reactors and thereby cracking, or splitting, their large molecules into the smaller ones that form the lighter, more valuable fractions such as gasoline, kerosene, and light industrial fuels. Gasoline manufactured by the cracking process performed better in automobile engines than gasoline derived from straight distillation of crude petroleum. The development of more powerful airplane engines in the late 1930s gave rise to a need to increase the combustion characteristics of gasoline and spurred the development of lead-based fuel additives to improve engine performance.

During the 1930s and World War II, sophisticated refining processes involving the use of catalysts led to further improvements in the quality of transportation fuels and further increased their supply. These improved processes—including catalytic cracking of heavy oils, alkylation, polymerization, and isomerization—enabled the petroleum industry to meet the demands of high-performance combat aircraft and, after the war, to supply increasing quantities of transportation fuels.

The 1950s and '60s brought a large-scale demand for jet fuel and high-quality lubricating oils. The continuing increase in demand for petroleum products also heightened the need to process a wider variety of crude oils into high-quality products. Catalytic reforming of naphtha replaced the earlier thermal reforming process and became the leading process for upgrading fuel qualities to meet the needs of higher-compression engines. Hydrocracking, a catalytic cracking process conducted in the presence of hydrogen, was developed to be a versatile manufacturing process for increasing the yields of either gasoline or jet fuels.

- Kerosene
- Diesel oils
- Fuel oils
- Lubricating oils
- Gear oils and greases
- Other petroleum products
- Petrochemicals
- Olefins
- Aromatics
- Polymers
- Inorganic chemicals
- Refinery plant and facilities
- Processing configurations
- Topping and hydroskimming refineries
- Conversion refineries
- Off-sites
- Tankage
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## ENVIRONMENTAL CONCERNS

By 1970 the petroleum-refining industry had become well established throughout the world. Delivery of crude oil to be refined into petroleum products had reached almost 2.3 billion tons per year (40 million barrels per day), with major concentrations of refineries in most developed countries. As the world became aware of the impact of industrial pollution on the environment, however, the petroleum-refining industry was a primary focus for change. Refiners added hydrotreating units to extract sulfur compounds from their products and began to generate large quantities of elemental sulfur. Effluent water and atmospheric emission of hydrocarbons and combustion products also became a focus of increased technical attention. In addition, many refined products came under scrutiny. Beginning in the mid-1970s, petroleum refiners in the United States and then around the world were required to develop techniques for manufacturing high-quality gasoline without employing lead additives, and beginning in the 1990s they were required to take on substantial investments in the complete reformulation of transportation fuels in order to minimize environmental emissions. From an industry that at one time produced a single product (kerosene) and disposed of unwanted by-product materials in any manner possible, petroleum refining has become one of the world's most stringently regulated manufacturing industries, expending a major portion of its resources on reducing its impact on the environment as it processes some 4.6 billion tons of crude oil per year (roughly 80 million barrels per day).

## RAW MATERIALS

### HYDROCARBON CHEMISTRY

Petroleum crude oils are complex mixtures of hydrocarbons, chemical compounds composed only of carbon (C) and hydrogen (H).

#### SATURATED MOLECULES

The simplest of the hydrocarbon molecules is methane ( $\text{CH}_4$ ), which has one carbon atom and four hydrogen atoms per molecule. The next simplest, ethane ( $\text{C}_2\text{H}_6$ ), has two carbon atoms and six hydrogen atoms. A whole class of hydrocarbons can be defined by expanding upon the relationship between methane and ethane. Known as the paraffins, this is a family of chainlike molecules with the chemical formula  $\text{C}_n\text{H}_{2n+2}$ . These molecules are also referred to as saturated, since each of the four valence electrons on a carbon atom that are available for bonding is taken up by a single hydrogen or carbon atom. Because these "single" bonds leave no valence electron available for sharing with another atom, paraffin molecules tend to be chemically stable.

Paraffins can be arranged either in straight chains (normal paraffins, such as butane; *see* figure) or branched chains (isoparaffins). Most of the paraffin compounds in naturally occurring crude oils are normal paraffins, while isoparaffins are frequently produced in refinery processes. The normal paraffins are uniquely poor as motor fuels, while isoparaffins have good engine-combustion characteristics. Longer-chain paraffins are major constituents of waxes.

Once a hydrocarbon molecule contains more than four carbon atoms, the carbon atoms may form not a branched or straight chain but a closed-ring structure known as a cyclo-compound. Saturated cyclo-compounds are called naphthenes. Naphthenic crudes tend to be poor raw materials for lubricant manufacture, but they are more easily converted into high-quality gasolines than are the paraffin compounds.

#### UNSATURATED MOLECULES

Two other chemical families that are important in petroleum refining are composed of unsaturated molecules. In unsaturated molecules, not all the valence electrons on a carbon atom are bonded to separate carbon or hydrogen atoms; instead, two or three electrons may be taken up by one neighbouring carbon atom, thus forming a "double" or "triple" carbon-carbon bond. Like saturated compounds, unsaturated compounds can form either chain or ring molecules. Unsaturated chain molecules are known as olefins. Only small amounts of olefins are found in crude oils, but large volumes are produced in refining processes. Olefins are relatively reactive as chemicals and can be readily combined to form other longer-chain compounds.

The other family of unsaturated compounds is made up of ring molecules called aromatics. The simplest aromatic compound, benzene ( $\text{C}_6\text{H}_6$ ), has double bonds linking every other carbon molecule (*see* figure). The double bonds in the benzene ring are very unstable and chemically reactive. Partly for this reason, benzene is a popular building block in the petrochemical industry.

Unsaturated hydrocarbons generally have good combustion characteristics, but their reactivity can lead to instability

in storage and sometimes to environmental emission problems.

## TYPES OF CRUDE OIL

The above description of hydrocarbons refers to simpler members of each family, but crude oils are actually complex mixtures of very long-chain compounds, some of which have not yet been identified. Because such complex mixtures cannot be readily identified by chemical composition, refiners customarily characterize crude oils by the type of hydrocarbon compound that is most prevalent in them: paraffins, naphthenes, and aromatics. Some crude oils, such as those in the original Pennsylvanian oil fields, consist mainly of paraffins. Others, such as the heavy Mexican and Venezuelan crudes, are predominantly naphthenic and are rich in bitumen (a high-boiling semisolid material).

The proportions of products that may be obtained by distillation of five typical crude oils, ranging from heavy Venezuelan Boscan to the light Bass Strait oil produced in Australia, are shown in the figure. Given the pattern of modern demand (which tends to be highest for transportation fuels such as gasoline), the market price of a crude oil generally rises with increasing yields of light products. It is possible to process heavier crudes more intensely in order to improve their yield of light products, but the capital and operating costs required to support such high conversion processes are much greater than those required to process lighter crudes into the same yield of products.

In addition to the hydrocarbons, compounds of sulfur, nitrogen, and oxygen are present in small amounts in crude oils. Also there are usually traces of vanadium, nickel, chlorine, sodium, and arsenic. These elements may affect the safety of oil-transport systems, the quality of refined products, and the effectiveness of processing units within a refinery. Minute traces can usually be tolerated, but crudes with larger amounts of these materials must be extensively treated in order to restrict their harmful effects.

## CONVENTIONAL MEASUREMENT SYSTEMS

Petroleum refining is a continuous manufacturing process that is highly dependent on careful measurement of operating variables to influence product qualities and to control operating expenses. The conventional practice for the industry in the United States is to measure capacity by volume and to employ the English system for other operating measurements. Most refiners in other areas of the world define capacity by the weight of materials processed and record operating measurements in metric units. Since many refiners throughout the world have U.S. shareholders, international results are often reported on both bases. In this article, all measurements will be presented in international terms with the U.S. equivalent indicated in parentheses.

### Measurement systems employed in petroleum refining

units of measure		
refinery operation	international	U.S.
quantity processed	metric tons	barrels (42 gallons per barrel)
unit capacity	tons per year	barrels per day
flow rate	cubic metres per day	barrels per day
temperature	degrees Celsius	degrees Fahrenheit
pressure	pascals or bars	pounds per square inch
heat energy	joules or calories	British thermal units

## BASIC REFINERY PROCESSES

Each refinery is uniquely designed to process specific crude oils into selected products. In order to meet the business objectives of the refinery, the process designer selects from an array of basic processing units. In general, these units perform one of three functions: (1) separating the many types of hydrocarbon present in crude oils into fractions of more closely related properties, (2) chemically converting the separated hydrocarbons into more desirable reaction products, and (3) purifying the products of unwanted elements and compounds.

## SEPARATION

### FRACTIONAL DISTILLATION

The primary process for separating the hydrocarbon components of crude oil is fractional distillation. Crude oil distillers separate crude oil into fractions for subsequent processing in such units as catalytic reformers, cracking units, alkylation units, or cokers. In turn, each of these more complex processing units also incorporates a fractional distillation tower to separate its own reaction products.

Modern crude oil distillation units operate continuously over long periods of time and are much larger than the fractional distillation units employed in chemical or other industries. Process rates are commonly delineated in American barrels; units capable of processing 100,000 barrels per day are commonplace, and the largest units are capable of charging more than 200,000 barrels per day.

The principles of operation of a modern crude oil distillation unit are shown in the figure. Crude oil is withdrawn from storage tanks at ambient temperature and pumped at a constant rate through a series of heat exchangers in order to reach a temperature of about 120 °C (250 °F). A controlled amount of fresh water is introduced, and the mixture is pumped into a desalting drum, where it passes through an electric field and a saltwater phase is separated. (If the salt were not removed at this stage, it would be deposited later on the tubes of the furnace and cause plugging.) The desalted crude oil passes through additional heat exchangers and then through steel alloy tubes in a furnace. There it is heated to a temperature between 315 and 400 °C (600 and 750 °F), depending on the type of crude oil and the end products desired. A mixture of vapour and unvaporized oil passes from the furnace into the fractionating column, a vertical cylindrical tower as much as 45 metres (150 feet) high containing 20 to 40 fractionating trays spaced at regular intervals. The most common fractionating trays are of the sieve or valve type. Sieve trays are simple perforated plates with small holes about 5 to 6 mm (0.2 to 0.25 inch) in diameter. Valve trays are similar, except the perforations are covered by small metal disks that restrict the flow through the perforations under certain process conditions.

The oil vapours rise up through the column and are condensed to a liquid in a water- or air-cooled condenser at the top of the tower. A small amount of gas remains uncondensed and is piped into the refinery fuel-gas system. A pressure control valve on the fuel-gas line maintains fractionating column pressure at the desired figure, usually near one standard atmosphere pressure, measured as approximately 1 bar, 100 kilopascals (KPa), or 15 pounds per square inch (psi). Part of the condensed liquid, called reflux, is pumped back into the top of the column and descends from tray to tray, contacting rising vapours as they pass through the slots in the trays. The liquid progressively absorbs heavier constituents from the vapour and, in turn, gives up lighter constituents to the vapour phase. Condensation and reevaporation takes place on each tray. Eventually an equilibrium is reached in which there is a continual gradation of temperature and oil properties throughout the column, with the lightest constituents on the top tray and the heaviest on the bottom. The use of reflux and vapour-liquid contacting trays distinguishes fractional distillation from simple distillation columns.

Intermediate products, or "sidestreams," are withdrawn at several points from the column, as shown in the figure. In addition, modern crude distillation units employ intermediate reflux streams. Sidestreams are known as intermediate products because they have properties between those of the top or overhead product and those of products issuing from the base of the column. Typical boiling ranges for various streams are as follows: light straight-run naphtha (overhead), 20–95 °C (70–200 °F); heavy naphtha (top sidestream), 90–165 °C (195– 330 °F); crude kerosene (second sidestream), 150–245 °C (300–475 °F); light gas oil (third sidestream), 215–315 °C (420–600 °F).

Unvaporized oil entering the column flows downward over a similar set of trays in the lower part of the column, called stripping trays, which act to remove any light constituents remaining in the liquid. Steam is injected into the bottom of the column in order to reduce the partial pressure of the hydrocarbons and assist in the separation. Typically a single sidestream is withdrawn from the stripping section: heavy gas oil, with a boiling range of 285–370 °C (545–700 °F). The residue that passes from the bottom of the column is suitable for blending into industrial fuels. Alternately, it may be further distilled under vacuum conditions to yield quantities of distilled oils for manufacture into lubricating oils or for use as a feedstock in a gas oil cracking process.

## VACUUM DISTILLATION

The principles of vacuum distillation resemble those of fractional distillation (commonly called atmospheric distillation to distinguish it from the vacuum method), except that larger-diameter columns are used to maintain comparable vapour velocities at reduced operating pressures. A vacuum of 50 to 100 mm of mercury absolute is produced by a vacuum pump or steam ejector.

The primary advantage of vacuum distillation is that it allows for distilling heavier materials at lower temperatures than those that would be required at atmospheric pressure, thus avoiding thermal cracking of the components. Firing conditions in the furnace are adjusted so that oil temperatures usually do not exceed 425 °C (800 °F). The residue remaining after vacuum distillation, called bitumen, may be further blended to produce road asphalt or residual fuel oil, or it may be used as a feedstock for thermal cracking or coking units. Vacuum distillation units are essential parts of the many processing schemes designed to produce lubricants.

## SUPERFRACTIONATION

An extension of the distillation process, superfractionation employs smaller-diameter columns with a much larger number of trays (100 or more) and reflux ratios exceeding 5:1. With such equipment it is possible to isolate a very narrow range of components or even pure compounds. Common applications involve the separation of high-purity solvents such as isoparaffins or of individual aromatic compounds for use as petrochemicals.

## ABSORPTION

Absorption processes are employed to recover valuable light components such as propane/propylene and butane/butylene from the vapours that leave the top of crude-oil or process-unit fractionating columns within the refinery. These volatile gases are bubbled through an absorption fluid, such as kerosene or heavy naphtha, in equipment resembling a fractionating column. The light products dissolve in the oil while the dry gases—such as hydrogen, methane, ethane, and ethylene—pass through undissolved. Absorption is more effective under pressures of about 7 to 10 bars (0.7 to 1 megapascal [MPa]), or 100 to 150 psi, than it is at atmospheric pressure.

The enriched absorption fluid is heated and passed into a stripping column, where the light product vapours pass upward and are condensed for recovery as liquefied petroleum gas (LPG). The unvaporized absorption fluid passes from the base of the stripping column and is reused in the absorption tower.

## SOLVENT EXTRACTION

Solvent extraction processes are employed primarily for the removal of constituents that would have an adverse effect on the performance of the product in use. An important application is the removal of heavy aromatic compounds from lubricating oils. Removal improves the viscosity-temperature relationship of the product, extending the temperature range over which satisfactory lubrication is obtained. The usual solvents for extraction of lubricating oil are phenol and furfural.

## ADSORPTION

Certain highly porous solid materials have the ability to select and adsorb specific types of molecules, thus separating them from other materials. Silica gel is used in this way to separate aromatics from other hydrocarbons, and activated charcoal is used to remove liquid components from gases. Adsorption is thus somewhat analogous to the process of absorption with an oil, although the principles are different. Layers of adsorbed material only a few molecules thick are formed on the extensive interior surface of the adsorbent; the interior surface may amount to several hectares per kilogram of material.

Molecular sieves are a special form of adsorbent. Such sieves are produced by the dehydration of naturally occurring or synthetic zeolites (crystalline alkali-metal aluminosilicates). The dehydration leaves intercrystalline cavities that have pore openings of definite size, depending on the alkali metal of the zeolite. Under adsorptive conditions, normal paraffin molecules can enter the crystalline lattice and be selectively retained, whereas all other molecules are excluded. This principle is used commercially for the removal of normal paraffins from gasoline fuels, thus improving their combustion properties. The use of molecular sieves is also extensive in the manufacture of high-purity solvents.

## CRYSTALLIZATION

The crystallization of wax from lubricating oil fractions is essential to make oils suitable for use. A solvent (often a mixture of benzene and methyl ethyl ketone) is first added to the oil, and the solution is chilled to about  $-20^{\circ}\text{C}$  ( $-5^{\circ}\text{F}$ ). The function of the benzene is to keep the oil in solution and maintain its fluidity at low temperatures, whereas the methyl ethyl ketone acts as a wax precipitant. Rotary filters deposit the wax crystals on a specially woven cloth stretched over a perforated cylindrical drum. A vacuum is maintained within the drum to draw the oil through the perforations. The wax crystals are removed from the cloth by metal scrapers, after washing with solvent to remove



traces of oil. The solvents are later distilled from the oil and reused.

## CONVERSION

The separation processes described above are based on differences in physical properties of the components of crude oil. All petroleum refineries throughout the world employ at least crude oil distillation units to separate naturally occurring fractions for further use, but those which employ distillation alone are limited in their yield of valuable transportation fuels. By adding more complex conversion processes that chemically change the molecular structure of naturally occurring components of crude oil, it is possible to increase the yield of valuable hydrocarbon compounds.

## NAPHTHA REFORMING

The most widespread process for rearranging hydrocarbon molecules is naphtha reforming. The initial process, thermal reforming, was developed in the late 1920s. Thermal reforming employed temperatures of 510–565 °C (950–1,050 °F) at moderate pressures—about 40 bars (4 MPa), or 600 psi—to obtain gasolines (petrols) with octane numbers of 70 to 80 from heavy naphthas with octane numbers of less than 40. The product yield, although of a higher octane level, included olefins, diolefins, and aromatic compounds. It was therefore inherently unstable in storage and tended to form heavy polymers and gums, which caused combustion problems.

By 1950 a reforming process was introduced that employed a catalyst to improve the yield of the most desirable gasoline components while minimizing the formation of unwanted heavy products and coke. (A catalyst is a substance that promotes a chemical reaction but does not take part in it.) In catalytic reforming, as in thermal reforming, a naphtha-type material serves as the feedstock, but the reactions are carried out in the presence of hydrogen, which inhibits the formation of unstable unsaturated compounds that polymerize into higher-boiling materials.

In most catalytic reforming processes, platinum is the active catalyst; it is distributed on the surface of an aluminum oxide carrier. Small amounts of rhenium, chlorine, and fluorine act as catalyst promoters. In spite of the high cost of platinum, the process is economical because of the long life of the catalyst and the high quality and yield of the products obtained. The principal reactions involve the breaking down of long-chain hydrocarbons into smaller saturated chains and the formation of isoparaffins, made up of branched-chain molecules. Formation of ring compounds (technically, the cyclization of paraffins into naphthenes) also takes place, and the naphthenes are then dehydrogenated into aromatic compounds (ring-shaped unsaturated compounds with fewer hydrogen atoms bonded to the carbon). The hydrogen liberated in this process forms a valuable by-product of catalytic reforming. The desirable end products are isoparaffins and aromatics, both having high octane numbers.

In a typical reforming unit the naphtha charge is first passed over a catalyst bed in the presence of hydrogen to remove any sulfur impurities. The desulfurized feed is then mixed with hydrogen (about five molecules of hydrogen to one of hydrocarbon) and heated to a temperature of 500–540 °C (930–1,000 °F). The gaseous mixture passes downward through catalyst pellets in a series of three or more reactor vessels. Early reactors were designed to operate at about 25 bars (2.5 MPa), or 350 psi, but current units frequently operate at less than 7 bars (0.7 MPa), or 100 psi. Because heat is absorbed in reforming reactions, the mixture must be reheated in intermediate furnaces between the reactors.

After leaving the final reactor, the product is condensed to a liquid, separated from the hydrogen stream, and passed to a fractionating column, where the light hydrocarbons produced in the reactors are removed by distillation.



The reformat product is then available for blending into gasoline without further treatment. The hydrogen leaving the product separator is compressed and returned to the reactor system.

Operating conditions are set to obtain the required octane level, usually between 90 and 100. At the higher octane levels, product yields are smaller, and more frequent catalyst regenerations are required. During the course of the reforming process, minute amounts of carbon are deposited on the catalyst, causing a gradual deterioration of the product yield pattern. Some units are semiregenerative facilities—that is, they must be removed from service periodically (once or twice annually) to burn off the carbon and rejuvenate the catalyst system—but increased demand for high-octane fuels has also led to the development of continuous regeneration systems, which avoid the periodic unit shutdowns and maximize the yield of high-octane reformat. Continuous regeneration employs a moving bed of catalyst particles that is gradually withdrawn from the reactor system and passed through a regenerator vessel, where the carbon is removed and the catalyst rejuvenated for reintroduction to the reactor system.

## CATALYTIC CRACKING

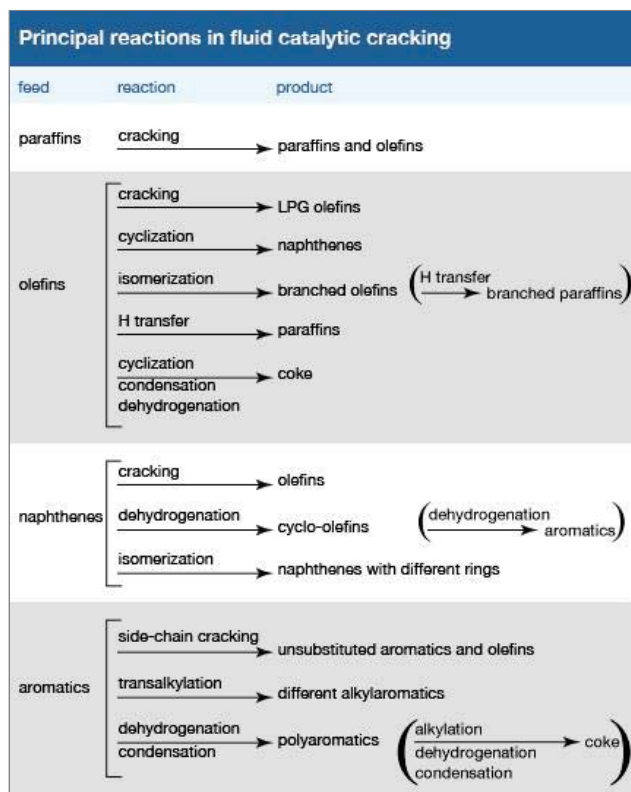
The use of thermal cracking units to convert gas oils into naphtha dates from before 1920. These units produced small quantities of unstable naphthas and large amounts of by-product coke. While they succeeded in providing a small increase in gasoline yields, it was the commercialization of the fluid catalytic cracking process in 1942 that really established the foundation of modern petroleum refining. The process not only provided a highly efficient means of converting high-boiling gas oils into naphtha to meet the rising demand for high-octane gasoline, but it also represented a breakthrough in catalyst technology.

The thermal cracking process functioned largely in accordance with the free-radical theory of molecular transformation. Under conditions of extreme heat, the electron bond between carbon atoms in a hydrocarbon molecule can be broken, thus generating a hydrocarbon group with an unpaired electron. This negatively charged molecule, called a free radical, enters into reactions with other hydrocarbons, continually producing other free radicals via the transfer of negatively charged hydride ions ( $H^-$ ). Thus a chain reaction is established that leads to a reduction in molecular size, or “cracking,” of components of the original feedstock.

Use of a catalyst in the cracking reaction increases the yield of high-quality products under much less severe operating conditions than in thermal cracking. Several complex reactions are involved, but the principal mechanism by which long-chain hydrocarbons are cracked into lighter products can be explained by the carbonium ion theory. According to this theory, a catalyst promotes the removal of a negatively charged hydride ion from a paraffin compound or the addition of a positively charged proton ( $H^+$ ) to an olefin compound. This results in the formation of a carbonium ion, a positively charged molecule that has only a very short life as an intermediate compound which transfers the positive charge through the hydrocarbon. Carbonium transfer continues as hydrocarbon compounds come into contact with active sites on the surface of the catalyst that promote the continued addition of protons or removal of hydride ions. The result is a weakening of carbon-carbon bonds in many of the hydrocarbon molecules and a consequent cracking into smaller compounds.

Olefins crack more readily than paraffins, since their double carbon-carbon bonds are more friable under reaction conditions. Isoparaffins and naphthenes crack more readily than normal paraffins, which in turn crack faster than aromatics. In fact, aromatic ring compounds are very resistant to cracking, since they readily deactivate fluid cracking catalysts by blocking the active sites of the catalyst. The table illustrates many of the principal reactions that are believed to occur in fluid catalytic cracking unit reactors. The reactions postulated for olefin compounds apply principally to intermediate products within the reactor system, since the olefin content of catalytic cracking

feedstock is usually very low.



Typical modern catalytic cracking reactors operate at 480–550 °C (900–1,020 °F) and at relatively low pressures of 0.7 to 1.4 bars (70 to 140 KPa), or 10 to 20 psi. At first natural silica-alumina clays were used as catalysts, but by the mid-1970s zeolitic and molecular sieve-based catalysts became common. Zeolitic catalysts give more selective yields of products while reducing the formation of gas and coke.

A modern fluid catalytic cracker employs a finely divided solid catalyst that has properties analogous to a liquid when it is agitated by air or oil vapours. The principles of operation of such a unit are shown in the figure. In this arrangement a reactor and regenerator are located side by side. The oil feed is vaporized when it meets the hot catalyst at the feed-injection point, and the vapours flow upward through the riser reactor at high velocity, providing a fluidizing effect for the catalyst particles. The catalytic reaction occurs exclusively in the riser reactor. The catalyst then passes into the cyclone vessel, where it is separated from reactor hydrocarbon products.

As the cracking reactions proceed, carbon is deposited on the catalyst particles. Since these deposits impair the reaction efficiency, the catalyst must be continuously withdrawn from the reaction system. Unit product vapours pass out of the top of the reactor through cyclone separators, but the catalyst is removed by centrifugal force and dropped back into the stripper section. In the stripping section, hydrocarbons are removed from the spent catalyst with steam, and the catalyst is transferred through the stripper standpipe to the regenerator vessel, where the carbon is burned with a current of air. The high temperature of the regeneration process (675–785 °C, or 1,250–1,450 °F) heats the catalyst to the desired reaction temperature for recontacting fresh feed into the unit. In order to maintain activity, a small amount of fresh catalyst is added to the system from time to time, and a similar amount is withdrawn.

The cracked reactor effluent is fractionated in a distillation column. The yield of light products (with boiling points

less than 220 °C, or 430 °F) is usually reported as the conversion level for the unit. Conversion levels average about 60 to 70 percent in Europe and Asia and in excess of 80 percent in many catalytic cracking units in the United States. About one-third of the product yield consists of fuel gas and other gaseous hydrocarbons. Half of this is usually propylene and butylene, which are important feedstocks for the polymerization and alkylation processes discussed below. The largest volume is usually cracked naphtha, an important gasoline blend stock with an octane number of 90 to 94. The lower conversion units of Europe and Asia produce comparatively more distillate oil and less naphtha and light hydrocarbons.

## POLYMERIZATION AND ALKYLATION

The light gaseous hydrocarbons produced by catalytic cracking are highly unsaturated and are usually converted into high-octane gasoline components in polymerization or alkylation processes. In polymerization, the light olefins propylene and butylene are induced to combine, or polymerize, into molecules of two or three times their original molecular weight. The catalysts employed consist of phosphoric acid on pellets of kieselguhr, a porous sedimentary rock. High pressures, on the order of 30 to 75 bars (3 to 7.5 MPa), or 400 to 1,100 psi, are required at temperatures ranging from 175 to 230 °C (350 to 450 °F). Polymer gasolines derived from propylene and butylene have octane numbers above 90.

The alkylation reaction also achieves a longer chain molecule by the combination of two smaller molecules, one being an olefin and the other an isoparaffin (usually isobutane). During World War II, alkylation became the main process for the manufacture of isooctane, a primary component in the blending of aviation gasoline.

Two alkylation processes employed in the industry are based upon different acid systems as catalysts. In sulfuric acid alkylation, concentrated sulfuric acid of 98 percent purity serves as the catalyst for a reaction that is carried out at 2 to 7 °C (35 to 45 °F). Refrigeration is necessary because of the heat generated by the reaction. The octane numbers of the alkylates produced range from 85 to 95.

Hydrofluoric acid is also used as a catalyst for many alkylation units. The chemical reactions are similar to those in the sulfuric acid process, but it is possible to use higher temperatures (between 24 and 46 °C, or 75 to 115 °F), thus avoiding the need for refrigeration. Recovery of hydrofluoric acid is accomplished by distillation. Stringent safety precautions must be exercised when using this highly corrosive and toxic substance.

## HYDROCRACKING

One of the most far-reaching developments of the refining industry in the 1950s was the use of hydrogen, made possible in part by the availability of hydrogen as a by-product of catalytic reforming. Since the 1980s hydrogen processing has become so prominent that many refineries now incorporate hydrogen-manufacturing plants in their processing schemes.

Though hydrocracking processes a similar feedstock to the catalytic cracking unit, it offers even greater flexibility in product yields. The process can be used for producing gasoline or jet fuels from heavy gas oils, for producing high-quality lubricating oils, or for converting distillation residues into lighter oils. The jet fuel and distillate oil products are of high quality and low sulfur content and may be blended into final products without further processing. Hydrocracked naphtha, on the other hand, is often low in octane and must be catalytically reformed to produce high-quality gasoline.

Hydrocracking is accomplished at lower temperatures than catalytic cracking—e.g., 260 to 425 °C (500 to 800 °F)—but at much higher pressures—55 to 170 bars (5.5 to 17 MPa), or 800 to 2,500 psi. The design and manufacture of large, thick-walled vessels for operation under these conditions has been a major engineering achievement.

Hydrocracking catalysts vary widely. The cracking reactions are induced by materials of the silica-alumina type. In units that process residual feedstocks, hydrogenation catalysts such as nickel, tungsten, platinum, or palladium are employed. The activity of the catalyst system can be maintained for long periods of time, so that continuous regeneration is not necessary as in catalytic cracking.

## ISOMERIZATION

The demand for aviation gasoline became so great during World War II and afterward that the quantities of isobutane available for alkylation feedstock were insufficient. This deficiency was remedied by isomerization of the more abundant normal butane into isobutane. The isomerization catalyst is aluminum chloride supported on alumina and promoted by hydrogen chloride gas.

Commercial processes have also been developed for the isomerization of low-octane normal pentane and normal hexane to the higher-octane isoparaffin form. Here the catalyst is usually promoted with platinum. As in catalytic reforming, the reactions are carried out in the presence of hydrogen. Hydrogen is neither produced nor consumed in the process but is employed to inhibit undesirable side reactions. The reactor step is usually followed by molecular sieve extraction and distillation. Though this process is an attractive way to exclude low-octane components from the gasoline blending pool, it does not produce a final product of sufficiently high octane to contribute much to the manufacture of unleaded gasoline.

## VISBREAKING, THERMAL CRACKING, AND COKING

Since World War II the demand for light products (e.g., gasoline, jet, and diesel fuels) has grown, while the requirement for heavy industrial fuel oils has declined. Furthermore, many of the new sources of crude petroleum (California, Alaska, Venezuela, and Mexico) have yielded heavier crude oils with higher natural yields of residual fuels. As a result, refiners have become even more dependent on the conversion of residue components into lighter oils that can serve as feedstock for catalytic cracking units.

As early as 1920, large volumes of residue were being processed in visbreakers or thermal cracking units. These simple process units basically consist of a large furnace that heats the feedstock to the range of 450 to 500 °C (840 to 930 °F) at an operating pressure of about 10 bars (1 MPa), or about 150 psi. The residence time in the furnace is carefully limited to prevent much of the reaction from taking place and clogging the furnace tubes. The heated feed is then charged to a reaction chamber, which is kept at a pressure high enough to permit cracking of the large molecules but restrict coke formation. From the reaction chamber the process fluid is cooled to inhibit further cracking and then charged to a distillation column for separation into components.

Visbreaking units typically convert about 15 percent of the feedstock to naphtha and diesel oils and produce a lower-viscosity residual fuel. Thermal cracking units provide more severe processing and often convert as much as 50 to 60 percent of the incoming feed to naphtha and light diesel oils.

Coking is severe thermal cracking. The residue feed is heated to about 475 to 520 °C (890 to 970 °F) in a furnace with

very low residence time and is discharged into the bottom of a large vessel called a coke drum for extensive and controlled cracking. The cracked lighter product rises to the top of the drum and is drawn off. It is then charged to the product fractionator for separation into naphtha, diesel oils, and heavy gas oils for further processing in the catalytic cracking unit. The heavier product remains and, because of the retained heat, cracks ultimately to coke, a solid carbonaceous substance akin to coal. Once the coke drum is filled with solid coke, it is removed from service and replaced by another coke drum.

Decoking is a routine daily occurrence accomplished by a high-pressure water jet. First the top and bottom heads of the coke drum are removed. Next a hole is drilled in the coke from the top to the bottom of the vessel. Then a rotating stem is lowered through the hole, spraying a water jet sideways. The high-pressure jet cuts the coke into lumps, which fall out the bottom of the drum for subsequent loading into trucks or railcars for shipment to customers. Typically, coke drums operate on 24-hour cycles, filling with coke over one 24-hour period followed by cooling, decoking, and reheating over the next 24 hours. The drilling derricks on top of the coke drums are a notable feature of the refinery skyline.

Cokers produce no liquid residue but yield up to 30 percent coke by weight. Much of the low-sulfur product is employed to produce electrodes for the electrolytic smelting of aluminum. Most lower-quality coke is burned as fuel in admixture with coal. Coker economics usually favour the conversion of residue into light products even if there is no market for the coke.

## PURIFICATION

Before petroleum products can be marketed, certain impurities must be removed or made less obnoxious. The most common impurities are sulfur compounds such as hydrogen sulfide ( $\text{H}_2\text{S}$ ) or the mercaptans ("R"SH)—the latter being a series of complex organic compounds having as many as six carbon atoms in the hydrocarbon radical ("R"). Apart from their foul odour, sulfur compounds are technically undesirable. In motor and aviation gasoline they reduce the effectiveness of antiknock additives and interfere with the operation of exhaust-treatment systems. In diesel fuel they cause engine corrosion and complicate exhaust-treatment systems. Also, many major residual and industrial fuel consumers are located in developed areas and are subject to restrictions on sulfurous emissions.

Most crude oils contain small amounts of hydrogen sulfide, but these levels may be increased by the decomposition of heavier sulfur compounds (such as the mercaptans) during refinery processing. The bulk of the hydrogen sulfide is contained in process-unit overhead gases, which are ultimately consumed in the refinery fuel system. In order to minimize noxious emissions, most refinery fuel gases are desulfurized.

Other undesirable components include nitrogen compounds, which poison catalyst systems, and oxygenated compounds, which can lead to colour formation and product instability. The principal treatment processes are outlined below.

## SWEETENING

Sweetening processes oxidize mercaptans into more innocuous disulfides, which remain in the product fuels. Catalysts assist in the oxidation. The doctor process employs sodium plumbite, a solution of lead oxide in caustic soda, as a catalyst. At one time this inexpensive process was widely practiced, but the necessity of adding elemental sulfur to make the reactions proceed caused an increase in total sulfur content in the product. It has largely been replaced by the copper chloride process, in which the catalyst is a slurry of copper chloride and fuller's earth. It is

applicable to both kerosene and gasoline. The oil is heated and brought into contact with the slurry while being agitated in a stream of air that oxidizes the mercaptans to disulfides. The slurry is then allowed to settle and is separated for reuse. A heater raises the temperature to a point that keeps the water formed in the reaction dissolved in the oil, so that the catalyst remains properly hydrated. After sweetening, the oil is water washed to remove any traces of catalyst and is later dried by passing through a salt filter.

## MERCAPTAN EXTRACTION

Simple sweetening is adequate for many purposes, but other methods must be used if the total sulfur content of the fuel is to be reduced. When solutizers, such as potassium isobutyrate and sodium cresylate, are added to caustic soda, the solubility of the higher mercaptans is increased and they can be extracted from the oil. In order to remove traces of hydrogen sulfide and alkyl phenols, the oil is first pretreated with caustic soda in a packed column or other mixing device. The mixture is allowed to settle and the product water washed before storage.

## CLAY TREATMENT

Some natural clays, activated by roasting or treatment with steam or acids, have been used for many years to remove traces of impurities. The phenomenon is similar to that described under the adsorption process: the clay retains the longer chain molecules within its highly porous structure.

Clay treatment removes gum and gum-forming materials from thermally cracked gasolines in the vapour phase. A more economical procedure, however, is to add small quantities of synthetic antioxidants to the gasoline. These prevent or greatly retard gum formation. Clay treatment of lubricating oils is widely practiced to remove resins and other colour bodies remaining after solvent extraction. The treatment may be by contact—that is, clay added directly to the oil, with the mixture heated and the clay filtered off—or by percolation, in which the heated oil is passed through a large bed of active clay adsorbent. The spent clay is often discarded, although it can be regenerated by roasting. However, the problem of dealing with spent clay, now designated as a hazardous waste in many places, has led many refiners to replace clay treatment facilities with a mild hydrogenation process.

## HYDROGEN TREATMENT

Hydrogen processes, commonly known as hydrotreating, are the most common processes for removing sulfur and nitrogen impurities. The oil is combined with high-purity hydrogen, vapourized, and then passed over a catalyst such as tungsten, nickel, or a mixture of cobalt and molybdenum oxides supported on an alumina base. Operating temperatures are usually between 260 and 425 °C (500 and 800 °F) at pressures of 14 to 70 bars (1.4 to 7 MPa), or 200 to 1,000 psi. Operating conditions are set to facilitate the desired level of sulfur removal without promoting any change to the other properties of the oil.

The sulfur in the oil is converted to hydrogen sulfide and the nitrogen to ammonia. The hydrogen sulfide is removed from the circulating hydrogen stream by absorption in a solution such as diethanolamine. The solution can then be heated to remove the sulfide and reused. The hydrogen sulfide recovered is useful for manufacturing elemental sulfur of high purity. The ammonia is recovered and either converted to elemental nitrogen and hydrogen, burned in the refinery fuel-gas system, or processed into agricultural fertilizers.

## MOLECULAR SIEVES

Molecular sieves are also used to purify petroleum products, since they have a strong affinity for polar compounds such as water, carbon dioxide, hydrogen sulfide, and mercaptans. Sieves are prepared by dehydration of an aluminosilicate such as zeolite. The petroleum product is passed through a bed of zeolite for a predetermined period depending on the impurity to be removed. The adsorbed contaminants may later be expelled from the sieve by purging with a gas stream at temperatures between 200 and 315 °C (400 and 600 °F). The frequent cycling of the molecular sieve from adsorb to desorb operations is usually fully automated.

## PETROLEUM PRODUCTS AND THEIR USES

### GASES

Gaseous refinery products include hydrogen, fuel gas, ethane, propane, and butane. Most of the hydrogen is consumed in refinery desulfurization facilities, which remove hydrogen sulfide from the gas stream and then separate that compound into elemental hydrogen and sulfur; small quantities of the hydrogen may be delivered to the refinery fuel system. Refinery fuel gas varies in composition but usually contains a significant amount of methane; it has a heating value similar to natural gas and is consumed in plant operations. Periodic variability in heating value makes it unsuitable for delivery to consumer gas systems. Ethane may be recovered from the refinery fuel system for use as a petrochemical feedstock. Propane and butane are sold as liquefied petroleum gas (LPG), which is a convenient portable fuel for domestic heating and cooking or for light industrial use.

### GASOLINE

Motor gasoline, or petrol, must meet three primary requirements. It must provide an even combustion pattern, start easily in cold weather, and meet prevailing environmental requirements.

### OCTANE RATING

In order to meet the first requirement, gasoline must burn smoothly in the engine without premature detonation, or knocking. Severe knocking can dissipate power output and even cause damage to the engine. When gasoline engines became more powerful in the 1920s, it was discovered that some fuels knocked more readily than others. Experimental studies led to the determination that, of the standard fuels available at the time, the most extreme knock was produced by a fuel composed of pure normal heptane, while the least knock was produced by pure isooctane. This discovery led to the development of the octane scale for defining gasoline quality. Thus, when a motor gasoline gives the same performance in a standard knock engine as a mixture of 90 percent isooctane and 10 percent normal heptane, it is given an octane rating of 90.

There are two methods for carrying out the knock engine test. Research octane is measured under mild conditions of temperature and engine speed (49 °C [120 °F] and 600 revolutions per minute, or RPM), while motor octane is measured under more severe conditions (149 °C [300 °F] and 900 RPM). For many years the research octane number was found to be the more accurate measure of engine performance and was usually quoted alone. Since the advent of unleaded fuels in the mid-1970s, however, motor octane measurements have frequently been found to limit actual engine performance. As a result a new measurement, road octane number, which is a simple average of the research and motor values, is most frequently used to define fuel quality for the consumer. Automotive gasolines generally range from research octane number 87 to 100, while gasoline for piston-engine aircraft ranges from research octane number 115 to 130.



Each naphtha component that is blended into gasoline is tested separately for its octane rating. Reformate, alkylate, polymer, and cracked naphtha, as well as butane, all rank high (90 or higher) on this scale, while straight-run naphtha may rank at 70 or less. In the 1920s it was discovered that the addition of tetraethyl lead would substantially enhance the octane rating of various naphthas. Each naphtha component was found to have a unique response to lead additives, some combinations being found to be synergistic and others antagonistic. This gave rise to very sophisticated techniques for designing the optimal blends of available components into desired grades of gasoline.

The advent of leaded, or ethyl, gasoline led to the manufacture of high-octane fuels and became universally employed throughout the world after World War II. However, beginning in 1975, environmental legislation began to restrict the use of lead additives in automotive gasoline. It is now banned in the United States, the European Union, and many countries around the world. The required use of lead-free gasoline has placed a premium on the construction of new catalytic reformers and alkylation units for increasing yields of high-octane gasoline ingredients and on the exclusion of low-octane naphthas from the gasoline blend.

## HIGH-VOLATILE AND LOW-VOLATILE COMPONENTS

The second major criterion for gasoline—that the fuel be sufficiently volatile to enable the car engine to start quickly in cold weather—is accomplished by the addition of butane, a very low-boiling paraffin, to the gasoline blend. Fortunately, butane is also a high-octane component with little alternate economic use, so its application has historically been maximized in gasoline. Another requirement, that a quality gasoline have a high energy content, has traditionally been satisfied by including higher-boiling components in the blend. However, both of these practices are now called into question on environmental grounds. The same high volatility that provides good starting characteristics in cold weather can lead to high evaporative losses of gasoline during refueling operations, and the inclusion of high-boiling components to increase the energy content of the gasoline can also increase the emission of unburned hydrocarbons from engines on start-up. As a result, since the 1990 amendments of the U.S. Clean Air Act, much of the gasoline consumed in urban areas of the United States has been reformulated to meet stringent new environmental standards. At first these changes required that gasoline contain certain percentages of oxygen in order to aid in fuel combustion and reduce the emission of carbon monoxide and nitrogen oxides. Refiners met this obligation by including some oxygenated compounds such as ethyl alcohol or methyl tertiary butyl ether (MTBE) in their blends. However, MTBE was soon judged to be a hazardous pollutant of groundwater in some cases where reformulated gasoline leaked from transmission pipelines or underground storage tanks, and it was banned in several parts of the country. In 2005 the requirements for specific oxygen levels were removed from gasoline regulations, and MTBE ceased to be used in reformulated gasoline. Many blends in the United States contain significant amounts of ethyl alcohol in order to meet emissions requirements, and MTBE is still added to gasoline in other parts of the world.

## GASOLINE BLENDING

One of the most critical economic issues for a petroleum refiner is selecting the optimal combination of components to produce final gasoline products. Gasoline blending is much more complicated than a simple mixing of components. First, a typical refinery may have as many as 8 to 15 different hydrocarbon streams to consider as blend stocks. These may range from butane, the most volatile component, to a heavy naphtha and include several gasoline naphthas from crude distillation, catalytic cracking, and thermal processing units in addition to alkylate, polymer, and reformate. Modern gasoline may be blended to meet simultaneously 10 to 15 different quality specifications, such as vapour pressure; initial, intermediate, and final boiling points; sulfur content; colour; stability; aromatics content; olefin content; octane measurements for several different portions of the blend; and other local

governmental or market restrictions. Since each of the individual components contributes uniquely in each of these quality areas and each bears a different cost of manufacture, the proper allocation of each component into its optimal disposition is of major economic importance. In order to address this problem, most refiners employ linear programming, a mathematical technique that permits the rapid selection of an optimal solution from a multiplicity of feasible alternative solutions. Each component is characterized by its specific properties and cost of manufacture, and each gasoline grade requirement is similarly defined by quality requirements and relative market value. The linear programming solution specifies the unique disposition of each component to achieve maximum operating profit. The next step is to measure carefully the rate of addition of each component to the blend and collect it in storage tanks for final inspection before delivering it for sale. Still, the problem is not fully resolved until the product is actually delivered into customers' tanks. Frequently, last-minute changes in shipping schedules or production qualities require the reblending of finished gasolines or the substitution of a high-quality (and therefore costlier) grade for one of more immediate demand even though it may generate less income for the refinery.

## KEROSENE

Though its use as an illuminant has greatly diminished, kerosene is still used extensively throughout the world in cooking and space heating and is the primary fuel for modern jet engines. When burned as a domestic fuel, kerosene must produce a flame free of smoke and odour. Standard laboratory procedures test these properties by burning the oil in special lamps. All kerosene fuels must satisfy minimum flash-point specifications (49 °C, or 120 °F) to limit fire hazards in storage and handling.

Jet fuels must burn cleanly and remain fluid and free from wax particles at the low temperatures experienced in high-altitude flight. The conventional freeze-point specification for commercial jet fuel is -50 °C (-58 °F). The fuel must also be free of any suspended water particles that might cause blockage of the fuel system with ice particles. Special-purpose military jet fuels have even more stringent specifications.

## DIESEL OILS

The principal end use of gas oil is as diesel fuel for powering automobile, truck, bus, and railway engines. In a diesel engine, combustion is induced by the heat of compression of the air in the cylinder under compression. Detonation, which leads to harmful knocking in a gasoline engine, is a necessity for the diesel engine. A good diesel fuel starts to burn at several locations within the cylinder after the fuel is injected. Once the flame has initiated, any more fuel entering the cylinder ignites at once.

Straight-chain hydrocarbons make the best diesel fuels. In order to have a standard reference scale, the oil is matched against blends of cetane (normal hexadecane) and alpha methyl-naphthalene, the latter of which gives very poor engine performance. High-quality diesel fuels have cetane ratings of about 50, giving the same combustion characteristics as a 50-50 mixture of the standard fuels. The large, slower engines in ships and stationary power plants can tolerate even heavier diesel oils. The more viscous marine diesel oils are heated to permit easy pumping and to give the correct viscosity at the fuel injectors for good combustion.

Until the early 1990s, standards for diesel fuel quality were not particularly stringent. A minimum cetane number was critical for transportation uses, but sulfur levels of 5,000 parts per million (ppm) were common in most markets. With the advent of more stringent exhaust emission controls, however, diesel fuel qualities came under increased scrutiny. In the European Union and the United States, diesel fuel is now generally restricted to maximum sulfur levels of 10 to 15 ppm, and regulations have restricted aromatic content as well. The limitation of aromatic compounds requires a much more demanding scheme of processing individual gas oil components than was

necessary for earlier highway diesel fuels.

## FUEL OILS

Furnace oil consists largely of residues from crude oil refining. These are blended with other suitable gas oil fractions in order to achieve the viscosity required for convenient handling. As a residue product, fuel oil is the only refined product of significant quantity that commands a market price lower than the cost of crude oil.

Because the sulfur contained in the crude oil is concentrated in the residue material, fuel oil sulfur levels are naturally high. The sulfur level is not critical to the combustion process as long as the flue gases do not impinge on cool surfaces (which could lead to corrosion by the condensation of acidic sulfur trioxide). However, in order to reduce air pollution, most industrialized countries now restrict the sulfur content of fuel oils. Such regulation has led to the construction of residual desulfurization units or cokers in refineries that produce these fuels.

Residual fuels may contain large quantities of heavy metals such as nickel and vanadium; these produce ash upon burning and can foul burner systems. Such contaminants are not easily removed and usually lead to lower market prices for fuel oils with high metal contents.

## LUBRICATING OILS

At one time the suitability of petroleum fractions for use as lubricants depended entirely on the crude oils from which they were derived. Those from Pennsylvania crude, which were largely paraffinic in nature, were recognized as having superior properties. But, with the advent of solvent extraction and hydrocracking, the choice of raw materials has been considerably extended.

Viscosity is the basic property by which lubricating oils are classified. The requirements vary from a very thin oil needed for the high-speed spindles of textile machinery to the viscous, tacky materials applied to open gears or wire ropes. Between these extremes is a wide range of products with special characteristics. Automotive oils represent the largest product segment in the market. In the United States, specifications for these products are defined by the Society of Automotive Engineers (SAE), which issues viscosity ratings with numbers that range from 5 to 50. In the United Kingdom, standards are set by the Institute of Petroleum, which conducts tests that are virtually identical to those of the SAE.

When ordinary mineral oils having satisfactory lubricity at low temperatures are used over an extended temperature range, excessive thinning occurs, and the lubricating properties are found to be inadequate at higher temperatures. To correct this, multigrade oils have been developed using long-chain polymers. Thus, an oil designated SAE 10W40 has the viscosity of an SAE 10W oil at  $-18^{\circ}\text{C}$  ( $0^{\circ}\text{F}$ ) and of an SAE 40 oil at  $99^{\circ}\text{C}$  ( $210^{\circ}\text{F}$ ). Such an oil performs well under cold starting conditions in winter (hence the W designation) yet will lubricate under high-temperature running conditions in the summer as well. Other additives that improve the performance of lubricating oils are antioxidants and detergents, which maintain engine cleanliness and keep fine carbon particles suspended in the circulating oil.

## GEAR OILS AND GREASES

In gear lubrication the oil separates metal surfaces, reducing friction and wear. Extreme pressures develop in some gears, and special additives must be employed to prevent the seizing of the metal surfaces. These oils contain sulfur compounds that form a resistant film on the surfaces, preventing actual metal-to-metal contact.

Greases are lubricating oils to which thickening agents are added. Soaps of aluminum, calcium, lithium, and sodium are commonly used, while nonsoap thickeners such as carbon, silica, and polyethylene also are employed for special purposes.

## OTHER PETROLEUM PRODUCTS

Highly purified naphthas are used for solvents in paints, cosmetics, commercial dry cleaning, and industrial product manufacture. Petroleum waxes are employed in paper manufacture and foodstuffs.

Asphaltic bitumen is widely used for the construction of roads and airfields. Specialized applications of bitumen also include the manufacture of roofing felts, waterproof papers, pipeline coatings, and electrical insulation. Carbon black is manufactured by decomposing liquid hydrocarbon fractions. It is compounded with rubber in tire manufacture and is a constituent of printing inks and lacquers.

## PETROCHEMICALS

By definition, petrochemicals are simply chemicals that happen to be derived from a starting material obtained from petroleum. They are, in almost every case, virtually identical to the same chemical produced from other sources, such as coal, coke, or fermentation processes.

## OLEFINS

The thermal cracking processes developed for refinery processing in the 1920s were focused primarily on increasing the quantity and quality of gasoline components. As a by-product of this process, gases were produced that included a significant proportion of lower-molecular-weight olefins, particularly ethylene, propylene, and butylene. Catalytic cracking is also a valuable source of propylene and butylene, but it does not account for a very significant yield of ethylene, the most important of the petrochemical building blocks. Ethylene is polymerized to produce polyethylene or, in combination with propylene, to produce copolymers that are used extensively in food-packaging wraps, plastic household goods, or building materials.

Ethylene manufacture via the steam cracking process is in widespread practice throughout the world. The operating facilities are similar to gas oil cracking units, operating at temperatures of 840 °C (1,550 °F) and at low pressures of 165 kilopascals (24 pounds per square inch). Steam is added to the vaporized feed to achieve a 50-50 mixture, and furnace residence times are only 0.2 to 0.5 second. In the United States and the Middle East, ethane extracted from natural gas is the predominant feedstock for ethylene cracking units. Propylene and butylene are largely derived from catalytic cracking units in the United States. In Europe and Japan, catalytic cracking is less common, and natural gas supplies are not as plentiful. As a result, both the Europeans and Japanese generally crack a naphtha or light gas oil fraction to produce a full range of olefin products.

## AROMATICS

The aromatic compounds, produced in the catalytic reforming of naphtha, are major sources of petrochemical products. In the traditional chemical industry, aromatics such as benzene, toluene, and the xylenes were made from coal during the course of carbonization in the production of coke and town gas. Today a much larger volume of these chemicals are made as refinery by-products. A further source of supply is the aromatic-rich liquid fraction

produced in the cracking of naphtha or light gas oils during the manufacture of ethylene and other olefins.

## **POLYMERS**

A highly significant proportion of these basic petrochemicals is converted into plastics, synthetic rubbers, and synthetic fibres. Together these materials are known as polymers, because their molecules are high-molecular-weight compounds made up of repeated structural units that have combined chemically. The major products are polyethylene, polyvinyl chloride, and polystyrene, all derived from ethylene, and polypropylene, derived from monomer propylene. Major raw materials for synthetic rubbers include butadiene, ethylene, benzene, and propylene. Among synthetic fibres the polyesters, which are a combination of ethylene glycol and terephthalic acid (made from xylenes), are the most widely used. They account for about one-half of all synthetic fibres. The second major synthetic fibre is nylon, its most important raw material being benzene. Acrylic fibres, in which the major raw material is the propylene derivative acrylonitrile, make up most of the remainder of the synthetic fibres.

## **INORGANIC CHEMICALS**

Two prominent inorganic chemicals, ammonia and sulfur, are also derived in large part from petroleum. Ammonia production requires hydrogen from a hydrocarbon source. Traditionally, the hydrogen was produced from a coke and steam reaction, but today most ammonia is synthesized from liquid petroleum fractions, natural gas, or refinery gases. The sulfur removed from oil products in purification processes is ultimately recoverable as elemental sulfur or sulfuric acid. It has become an important source of sulfur for the manufacture of fertilizer.

## **REFINERY PLANT AND FACILITIES**

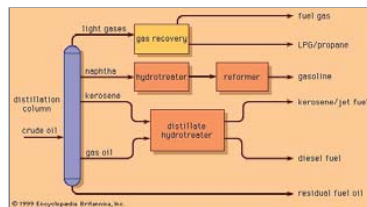
### **PROCESSING CONFIGURATIONS**

Each petroleum refinery is uniquely configured to process a specific raw material into a desired slate of products. In order to determine which configuration is most economical, engineers and planners survey the local market for petroleum products and assess the available raw materials. Since about half the product of fractional distillation is residual fuel oil, the local market for it is of utmost interest. In parts of Africa, South America, and Southeast Asia, heavy fuel oil is easily marketed, so that refineries of simple configuration may be sufficient to meet demand. However, in the United States, Canada, and Europe, large quantities of gasoline are in demand, and the market for fuel oil is constrained by environmental regulations and the availability of natural gas. In these places, more complex refineries are necessary.

### **TOPPING AND HYDROSKIMMING REFINERIES**

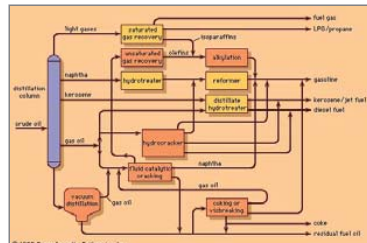
The simplest refinery configuration, called a topping refinery, is designed to prepare feedstocks for petrochemical manufacture or for production of industrial fuels in remote oil-production areas. It consists of tankage, a distillation unit, recovery facilities for gases and light hydrocarbons, and 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. Still, these refineries may produce up to half of their output as residual fuel oil, and they face increasing economic hardship as the demand for



Unit operations in a hydroskimming refinery. Nonshaded portions show the basic distillation ...

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Unit operations in a conversion refinery. Shaded portions indicate units added to a ...

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high-sulfur fuel oils declines.

## CONVERSION REFINERIES

The most versatile refinery configuration is known as the conversion refinery. A conversion refinery incorporates all the basic building blocks 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 gasoline, with the balance distributed between high-quality jet fuel, liquefied petroleum gas (LPG), diesel fuel, and a small quantity of petroleum coke. Many such refineries also incorporate solvent extraction processes for manufacturing lubricants and petrochemical units with which to recover high-purity propylene, benzene, toluene, and xylenes for further processing into polymers.

## OFF-SITES

The individual processing units described above are part of the process-unit side of a refinery complex. They are usually considered the most important features, but the functioning of the off-site facilities are often as critical as the process units themselves. Off-sites consist of tankage, flare systems, utilities, and environmental treatment units.

## TANKAGE



Oil refinery at Coryton, Thurrock, Essex, England.

Terry Joyce



Oil refinery in Esmeraldas, Ecuador.

KelvinLemos

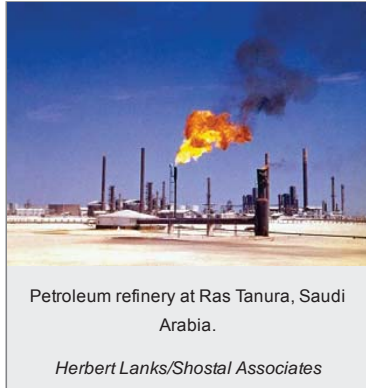
Refineries typically provide storage for raw materials and products that equal about 50 days of refinery throughput. Sufficient crude oil tankage must be available to allow for continuous refinery operation while still allowing for irregular arrival of crude shipments by pipeline or ocean-going tankers. The scheduling of tanker movements is particularly important for large refineries processing Middle Eastern crudes, which are commonly shipped in very large crude carriers (VLCCs) with capacities of 200,000 to 320,000 tons, or approximately two million barrels. Ultralarge crude carrier (ULCCs) can carry even more, surpassing 550,000 tons, or more than three million barrels. Generally, intermediate process streams and finished products require even more tankage than crude oil. In addition, provision must be made for short-term variations in demand for products and also for maintaining a dependable supply of products to the market during periods when process units must be removed from service for maintenance.

Nonvolatile products such as diesel fuel and fuel oils are stored in large-diameter cylindrical tanks with low-pitched conical roofs. Tanks with floating roofs reduce the evaporative losses in storage of gasolines and other volatile products, including crude oils. The roof, which resembles a pontoon, floats on the surface of the liquid within the tank, thus moving up and down with the liquid level and eliminating the air space that could contain petroleum



vapour. For LPG and butanes, pressure vessels (usually spherical) are used.

## FLARES



Petroleum refinery at Ras Tanura, Saudi Arabia.

*Herbert Lanks/Shostal Associates*

One of the prominent features of every oil refinery and petrochemical plant is a tall stack with a small flame burning at the top. This stack, called a flare, is an essential part of the plant safety system. In the event of equipment failure or plant shutdown, it is necessary to purge the volatile hydrocarbons from operating equipment so that it can be serviced. Since these volatile hydrocarbons form very explosive mixtures if they are mixed with air, as a safety precaution they are delivered by closed piping systems to the flare site, where they may be burned in a controlled manner. Under normal conditions only a pilot light is visible on the flare stack, and steam is often added to the flare to mask even that flame. However, during emergency conditions the flare system disposes of large quantities of volatile gases and illuminates the sky.

## UTILITIES

A typical refinery requires enough utilities to support a small city. All refineries produce steam for use in process units. This requires water-treatment systems, boilers, and extensive piping networks. Many refineries also produce electricity for lighting, electric motor-driven pumps, and compressors and instrumentation systems. In addition, clean, dry air must be provided for many process units, and large quantities of cooling water are required for condensation of hydrocarbon vapours.

## ENVIRONMENTAL TREATMENT

The large quantity of water required to support refinery operations must be treated to remove traces of hydrocarbons and noxious chemicals before it can be disposed of into waterways or underground disposal wells. In addition, each of the process units that vent hydrocarbons, flue gases, or particulate solids must be carefully monitored to ensure compliance with environmental standards. Finally, appropriate procedures must be employed to dispose of spent catalysts from refinery processing units.

## BULK TRANSPORTATION



Oil refinery at Coryton, Thurrock, Essex, England.

*Terry Joyce*

Large oceangoing tankers have sharply reduced the cost of transporting crude oil, making it practical to locate refineries near major market areas rather than adjacent to oil fields. To receive these large carriers, deepwater ports have been constructed in such cities as Rotterdam (Netherlands), Singapore, and Houston (Texas). Major refining centres are connected to these ports by pipelines.

Countries having navigable rivers or canals afford many opportunities for using barges, a very inexpensive method of transportation. The Mississippi River in the United States and the Rhine and Seine rivers in Europe are especially suited to

barges of more than 5,000 tons (37,000 barrels). Each barge may be divided into several compartments so that a variety of products may be carried.



Transport by railcar is still widely practiced, especially for specialty products such as LPG, lubricants, or asphalt. Cars have capacities exceeding 100 tons (720 barrels), depending on the product carried. The final stage of product delivery to the majority of customers throughout the world continues to be the familiar tanker truck, whose carrying capacity is about 150 to 200 barrels.



Section of the Trans-Alaska Pipeline,  
Alaska, U.S.

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The most efficient mode of bulk transport for petroleum is the network of pipelines that are now found all over the world. Most crude-oil-producing areas are connected by pipeline either to refining centres or to a maritime loading port. In addition, many major crude-oil-receiving ports have extensive pipeline distribution networks to inland refineries. Centrifugal pumps usually provide the pumping power, with booster stations installed along the line as necessary. Most of the major product lines have been converted to fully automated operation, with the opening and closing of valves carried out by automatic sequence controls initiated from remote control centres.

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