PETROLEUM: CHEMISTRY, REFINING, FUELS AND PETROCHEMICALS -REFINING

James G. Speight

2476 Overland Road,Laramie, WY 82070-4808, USA

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Contents

Summary

In the crude state petroleum has minimal value, but when refined it provides high-value liquid fuels, solvents, lubricants, and many other products. Refining petroleum involves subjecting the feedstock to a series of physical and chemical processes as a result of which a variety of products are generated. In some of the processes, e.g., distillation, the constituents of the feedstock are isolated unchanged, whereas in other processes, e.g., cracking, considerable changes are brought about to the constituents. Refinery processes must be selected and products 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. This section describes the processes by which refining occurs and the options that allow a refinery flexibility to treat a variety of feedstocks.

1. Introduction

Refining petroleum involves subjecting the feedstock to a series of physical and chemical processes as a result of which a variety of products are generated (Section 6.186R). In some of the processes, e.g., distillation, the constituents of the feedstock are isolated unchanged, whereas in other processes, e.g., cracking, considerable changes are brought about to the constituents. Intermediate products such as gas oil can even be reprocessed to break high molecular weight long-chained oil into a lighter short-chained one, by various forms of cracking such as *fluid catalytic cracking*, *thermal cracking*, and *hydrocracking*. The final step in gasoline production is the blending of fuels with different octane ratings, vapor pressures, and other properties to meet product specifications.

Auxiliary operations and facilities include: steam and power generation; process and fire water systems; flares and relief systems; furnaces and heaters; pumps and valves; supply of steam, air, nitrogen, and other plant gases; alarms and sensors; noise and pollution controls; sampling, testing, and inspecting; and laboratory, control room, maintenance, and administrative facilities.

Refinery processes must be selected and products 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 stocks and asphalt.

2. Dewatering and Desalting

Before separation of petroleum into its various constituents can proceed, there is the need to clean the petroleum. This is often referred to as de-salting and de-watering 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. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by desalting (dehydration).

Desalting is a water-washing operation performed at the production field and at the refinery site for additional crude oil cleanup (Figure 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 the contaminants are not removed, they can cause operating problems during refinery processing, such as equipment plugging and corrosion as well as catalyst deactivation duirng refining.
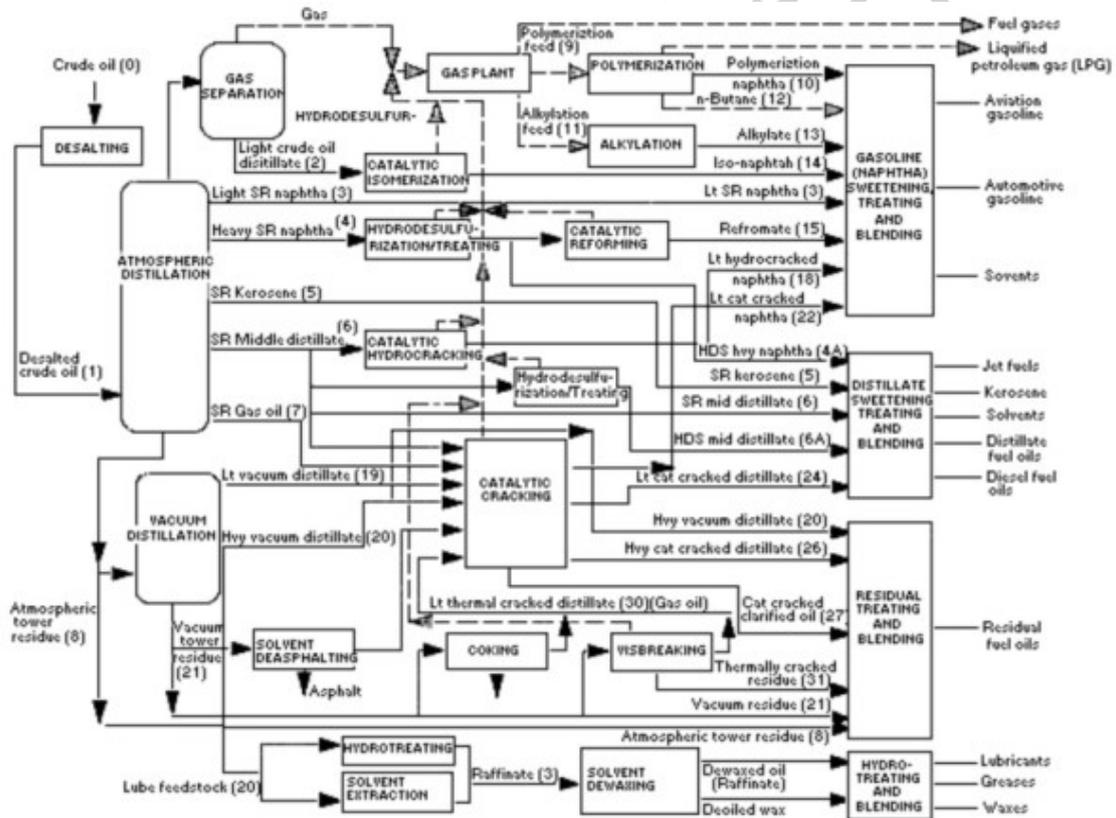
Figure 1. Schematic overview of a refinery.
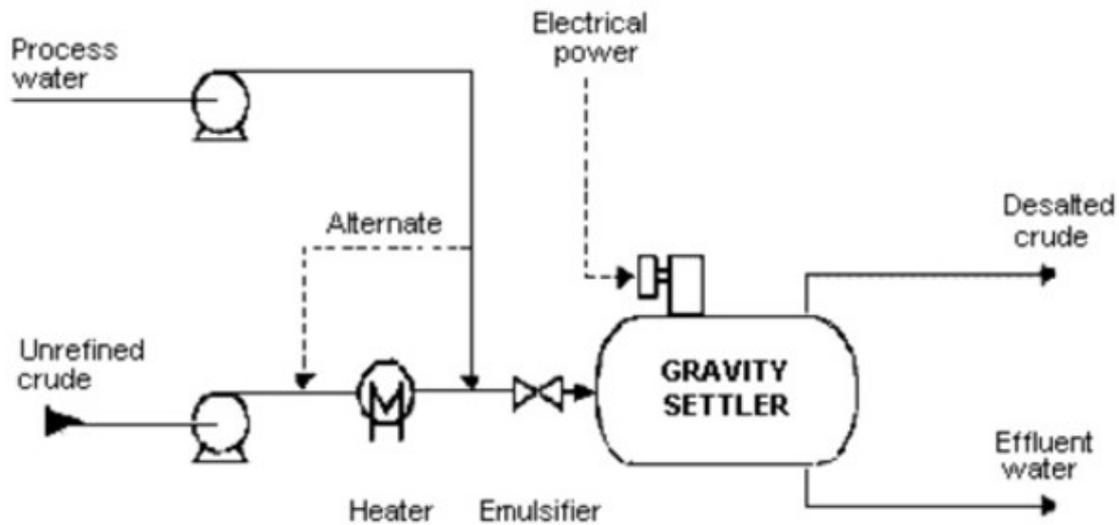
Figure 2. An electrostatic desalting unit.

The two most typical methods of crude-oil desalting, chemical and electrostatic separation, use hot water as the extraction agent. In chemical desalting, water and chemical surfactant (demulsifiers) are added to the crude, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they settle out. Electrical desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids. Both methods of desalting are continuous. A third and less-common process involves filtering heated crude using diatomaceous earth.

The feedstock crude oil is heated to between 150 and 350°F to reduce viscosity and surface tension for easier mixing and separation of the water. The temperature is limited by the vapor pressure of the crude-oil feedstock. In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash. Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower.

Inadequate desalting can cause fouling of heater tubes and heat exchangers throughout the refinery. Fouling restricts product flow and heat transfer and leads to failures due to increased pressures and temperatures. Corrosion, which occurs due to the presence of hydrogen sulfide, hydrogen chloride, naphthenic (organic) acids, and other contaminants in the crude oil, also causes equipment failure. Neutralized salts (ammonium chlorides and sulfides), when moistened by condensed water, can cause corrosion.

3. Distillation

The first step in the refining process proper is the separation of crude oil into various

fractions or straight-run cuts by distillation in atmospheric and vacuum towers. The main fractions or *cuts* obtained have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum.

3.1. Atmospheric Distillation

The present-day petroleum distillation unit is a collection of distillation units within the distillation tower (Figure 3).

The desalted crude oil is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater where it is fed into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 650 to 700°F (heating crude oil above these temperatures may cause undesirable thermal cracking). All but the highest molecular weight fractions flash into vapor. As the hot vapor rises in the tower, its temperature is reduced. Heavy fuel oil or asphalt residue is taken from the bottom. At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.
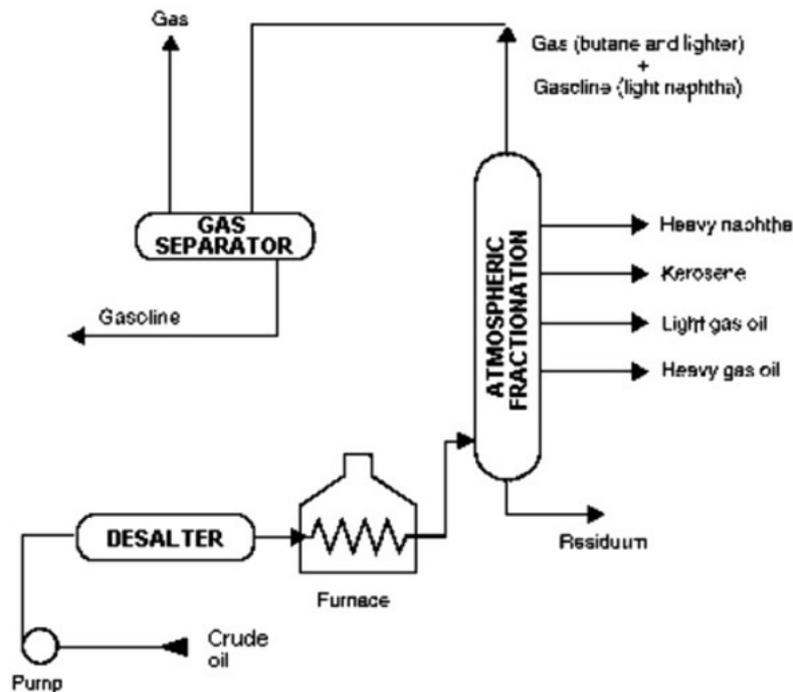

Figure 3. An atmospheric distillation unit.

The distillation 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. Here 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 vapors pass up the tower to be fractionated into gas oils, kerosene, and naphtha.

The fractionating tower, a steel cylinder up to 120 feet high, can accommodate 25,000 bbl, or more of crude petroleum per day. The tower contains horizontal steel trays for separating and collecting the liquids. At each tray, vapors from below enter perforations and bubble caps. They permit the vapors to bubble through the liquid on the tray, causing some condensation at the temperature of that tray. An overflow pipe drains the condensed liquids from each tray back to the tray below, where the higher temperature causes re-evaporation. The evaporation, condensing, and scrubbing operation are repeated many times until the desired degree of product purity is reached. Then side streams from certain trays are taken off to obtain the desired fractions. Products ranging from uncondensed fixed gases at the top to heavy fuel oils at the bottom can be taken continuously from a fractionating tower. Steam is often used in towers to lower the vapor pressure and create a partial vacuum. The distillation process separates the major constituents of crude oil into so-called straight-run products. Sometimes crude oil is "topped" by distilling off only the lighter fractions, leaving a heavy residue that is often distilled further under high vacuum.

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.

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

3.2. Vacuum Distillation

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) are usually 50 to 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 feet (14 meters). By this means, a heavy gas oil may be obtained as an overhead product at temperatures of about 150°C (300°F), and lubricating oil cuts may be obtained at temperatures of 250 to 350°C (480 to 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 is obtained as a side-stream 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.
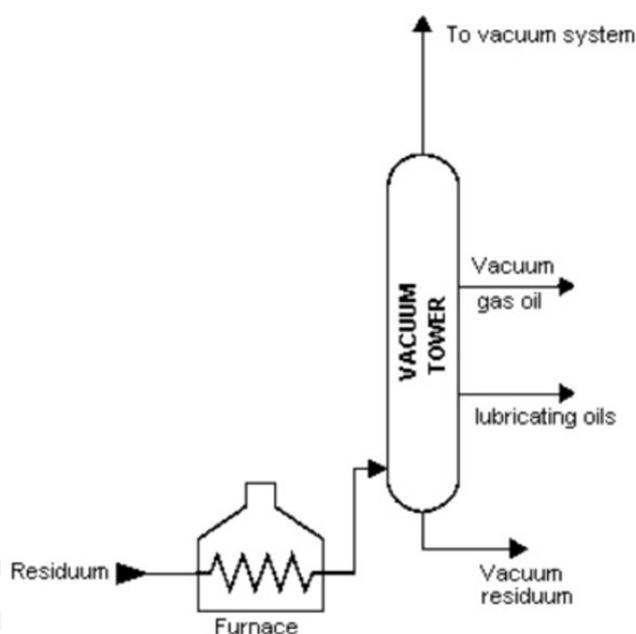

Figure 4. A vacuum distillation unit.

3.3. Azeotropic and Extractive Distillation

All compounds have definite boiling temperatures but a mixture of chemically dissimilar compounds will sometimes cause one or both of the components to boil at a temperature other than that expected. A mixture that boils at a temperature lower than the boiling point of any of the components is an azeotropic mixture. When it is desired to separate close-boiling components, the addition of a non-indigenous component will form an azeotropic mixture with one of the components of the mixture thereby lowering the boiling point by the formation of an *azeotrope* and facilitate separation by distillation.

The separation of these components of similar volatility may become economic if an *entrainer* can be found that effectively changes the relative volatility. It is also desirable

that the entrainer be reasonably cheap, stable, nontoxic, and readily recoverable from the components. In practice it is probably this last-named criterion that limits severely the application of extractive and azeotropic distillation. The majority of successful processes are those in which the entrainer and one of the components separate into two liquid phases on cooling if direct recovery by distillation is not feasible. A further restriction in the selection of an azeotropic entrainer is that the boiling point of the entrainer be in the range of 10 to 40°C (18 to 72°F) below that of the components.

4. Thermal Processes

Distillation of crude oil produces amounts and types of products that are not consistent with those required by the marketplace, subsequent refinery processes change the product mix by altering the molecular structure of the hydrocarbons. One of the ways of accomplishing this change is through *cracking* (thermal decomposition) the higher boiling-point petroleum fractions into more valuable products such as gasoline, fuel oil, and gas oils. The two basic types of cracking are thermal cracking, using heat and pressure, and catalytic cracking.

4.1. Thermal Cracking

The majority of the thermal cracking processes use temperatures of 455 to 540°C (850 to 1005°F) and pressures of 100 to 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.

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Biographical Sketch

Dr. Speight has more than thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research and development in refining heavy oil and coal, and related environmental issues. He has well over four hundred publications, reports, and presentations detailing these research activities and has taught more than forty related courses.

Dr. Speight is currently editor of the journal Petroleum Science and Technology (formerly Fuel Science and Technology International) and editor of the journal Energy Sources. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemical and Fuels Engineering at the University of Utah.

Dr. Speight is the author/editor/compiler of more than twenty books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, for Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996 for his Contributions to Coal Research. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia for Exceptional Work in Petroleum Science in 1997. In 2001, Dr. Speight was also awarded the Einstein Medal of the Russian Academy of Sciences (Natural) in recognition of Outstanding Contributions and Service in the field of Geologic Sciences.