Section II

Refining
7 Pretreatment and Distillation

7.1 INTRODUCTION

Petroleum in the unrefined state is of limited value and of limited use. Refining is required to produce products that are attractive to the marketplace. Thus, petroleum refining is a series of integrated steps by which the crude oil is converted into salable products with the desired qualities and in the amounts dictated by the market (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). In fact, a refinery is essentially a group of manufacturing plants that vary in number with the variety of products produced. Refinery processes must be selected and products manufactured to give a balanced operation. Crude oil must be converted into products according to the demand for each.

The petroleum refinery of the current century is a much more complex operation (Figure 7.1) than those refineries of the early 1900s and even of the immediate years following World War II (Jones, 1995; Speight, 2011, 2014a). Early refineries were predominantly distillation units, perhaps with ancillary units to remove objectionable odors from the various product streams. The refinery of the 1930s was somewhat more complex but was essentially a distillation unit (Speight, 2014a), but at this time cracking and coking units were starting to appear in the scheme of refinery operations. These units were not what we imagine today as a cracking and coking unit but were the forerunners of today’s units. Also at this time, asphalt was becoming a recognized petroleum product. Finally, current refineries (Figure 7.1) are a result of major evolutionary trends and are highly complex operations. Most of the evolutionary adjustments to refineries have occurred during the decades since the commencement of World War II. In the petroleum industry, as in many other industries, supply and demand are key factors in efficient and economic operation. Innovation is also a key.

A refinery is an integrated group of manufacturing plants (Figure 7.1) that vary in number with the variety of products produced. Refinery processes must be selected and products manufactured to give a balanced operation: that is, crude oil must be converted into products according to the rate of sale of 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, they accumulate until refinery storage facilities are full. To prevent the occurrence of such a situation, the refinery must be flexible and able to change operations as needed. This usually means more processes to accommodate the ever-changing demands of the market (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). This could be reflected in the inclusion of a cracking process to change an excess of heavy fuel oil into more gasoline with coke as the residual product or inclusion of a vacuum distillation process to separate the heavy oil into lubricating oil stocks and asphalt.

Thus, to accommodate the sudden changes in market demand, a refinery must include the following: (1) all necessary nonprocessing facilities; (2) adequate tank capacity for storing crude oil, intermediate, and finished products; (3) a dependable source of electrical power; (4) material-handling equipment; (5) workshops and supplies for maintaining a continuous 24 hours/day, 7 day/week operation; (6) waste disposal and water-treating equipment; and (7) and product-blending facilities (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

Petroleum refining is a very recent science and many innovations have evolved during the twentieth century. The purpose of this chapter is to illustrate the initial processes that are applied
to a feedstock in a refinery. The first processes (desalting and dewatering) focus on the cleanup of the feedstock, particularly the removal of the troublesome brine constituents (Burris, 1992). This is followed by distillation to remove the volatile constituents with the concurrent production of a residuum that can be used as a cracking (coking) feedstock or as a precursor to asphalt. Current methods of bitumen processing (Speight, 2000, 2014a) involve direct use of the bitumen as feedstock for delayed or fluid coking (Chapter 8). Other methods of feedstock treatment that involve the concept of volatility are also included here even though some of the methods (such as stripping, rerunning, and the like) might also be used for product purification. However, the distillation step is a viable step that produces additional valuable high-boiling fractions from the bitumen.
7.2 DEWATERING AND DESALTING

Even though distillation is, to all appearances, the first step in crude oil refining, it should be recognized that crude oil that is contaminated by salt water either from the well or during transportation to the refinery must be treated to remove the emulsion (Burris, 1992; Abdel-Aal et al., 2016). If salt water is not removed, the materials of construction of the heater tubes and column intervals are exposed to chloride ion attack and the corrosive action of hydrogen chloride, which may be formed at the temperature of the column feed.

Most crude oils contain traces of salt through the salt water produced with the crude feedstock (Speight, 2000, 2014a; Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007). Desalting operations are necessary to remove salt from the brines that are present with the crude oil after recovery (Abel-Aal et al., 2016). The salt can decompose in the heater to form hydrochloric acid and cause corrosion of the fractionator overhead equipment. In order to remove the salt, water is injected into the partially preheated crude, and the stream is thoroughly mixed so that the water extracts practically all the salt from the oil. The mixture of oil and water is separated in a desalter, which is a large vessel in which the water settles out of the oil, a process that may be accelerated by the addition of chemicals or by electrical devices. The salt-laden water is automatically drained from the bottom of the desalter. Failure to remove the brine to acceptable levels can result in unacceptable levels of hydrogen chloride produced during refining. The hydrogen chloride will cause corrosion to equipment even to the point of weakening the equipment and causing fires and explosions.

Generally, removal of this unwanted water has been fairly straightforward, involving wash tanks or a heater. Removal of this same water along with salt concentration reduction presents a completely different set of problems. These can be overcome with relative ease if the operator is willing to spend many thousands of dollars each year for water, fuel, power, and chemical additives. Conversely, if some time is spent in the initial design stages to determine the best methods for water removal to achieve lower bottom sediment and water (BS&W) remnants, mixing, and injection, then a system can be designed that will operate at a greatly reduced annual cost. In most cases, yearly savings on operational expenses will pay for the complete installation in 1–3 years.

The practice of desalting crude oil is an old process and can occur at the wellhead or (depending on the level of salt in the crude oil) at the refinery (Speight, 2000, 2014a; Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007). Indeed, refineries have been successfully desalting crude oil to less than 5 lb per thousand bbl for many years, and mechanical and electrostatic desalting have been improved greatly. However, very little attention has been given to the use of dilution water, probably due to the general availability of both freshwater and wastewater in and near refineries. Three general approaches have been taken to the desalting of crude petroleum (Figure 7.2). Numerous variations of each type have been devised, but the selection of a particular process depends on the type of salt dispersion and the properties of the crude oil.

The salt or brine suspensions may be removed from crude oil by heating (90°C–150°C, 200°F–300°F) under pressure (50–250 psi) that is sufficient to prevent vapor loss and then allowing the material to settle in a large vessel. Alternatively, coalescence is aided by passage through a tower packed with sand, gravel, and the like.

The common removal technique is to dilute the original brine with fresher water so that the salt content of water that remains after separation treatment is acceptable, perhaps 10 lb per thousand barrels of crude oil, or less. In areas where freshwater supplies are limited, the economics of this process can be critical. However, crude oil desalting techniques in the field have improved with the introduction of the electrostatic coalescing process (Figure 7.2). Even when adequate supplies of freshwater are available for desalting operations, preparation of the water for dilution purposes may still be expensive. Requirements for dilution water ratios based on water salinity calculations (Table 7.1; Figure 7.3) can be calculated as a material balance and by combining the arithmetic mean of material balance
and water injection and dispersion for contact efficiency, very low dilution water use rates can be achieved. This can be highly significant in an area where production rates of 100,000 bbl/day are common and freshwater supply is limited.

Desalter units generally will produce a dehydrated stream containing like amounts of bottom sediment and water (BS&W) from each stage. Therefore, bottom sediment and water can be considered as pass through volume, and the dilution water added is the amount of water to be recycled. The recycle pump, however, generally is oversized to compensate for difficult emulsion conditions and upsets in the system. Dilution water calculations for a two-stage system using recycle are slightly more complicated than for a single-stage process (Table 7.2; Figure 7.4) or a two-stage process without recycle (Table 7.3; Figure 7.5).

The common approach to desalting crude oil involves use of the two-stage desalting system (Figure 7.5) in which dilution water is injected between stages after the stream water content has been reduced to a very low level by the first stage. Further reduction is achieved by adding the second-stage recycle pump. The second-stage water is much lower in sodium chloride (NaCl) than the produced stream inlet water due to addition of dilution water. By recycling this water to the first stage, both salt reduction and dehydration are achieved in the first stage. The water volume to be recycled is assumed to be the same as dilution water injection volume.

A very low bottom sediment and water content at the first-stage desalter exit requires a high percentage of dilution water to properly contact dispersed, produced water droplets and achieve desired

---

**TABLE 7.1**

<table>
<thead>
<tr>
<th>Salt Content of Water (ppm)</th>
<th>Volume Percent Water Content in Oil (bbl Water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.00 (10)</td>
</tr>
<tr>
<td>10,000</td>
<td>35.00</td>
</tr>
<tr>
<td>20,000</td>
<td>70.00</td>
</tr>
<tr>
<td>30,000</td>
<td>105.00</td>
</tr>
<tr>
<td>40,000</td>
<td>140.00</td>
</tr>
<tr>
<td>50,000</td>
<td>175.00</td>
</tr>
<tr>
<td>100,000</td>
<td>350.00</td>
</tr>
<tr>
<td>150,000</td>
<td>525.00</td>
</tr>
<tr>
<td>200,000</td>
<td>700.00</td>
</tr>
</tbody>
</table>
Pretreatment and Distillation

Salt concentration reduction. This percentage dilution water varies with the strength of the water/oil emulsion and oil viscosity. Empirical data show that the range is from 4.0% to as high as 10%. Obviously, this indicates that the mixing efficiency of 80% is not valid when low water contents are present. Additional field data show that the use rates for the use of low dilution water can be maintained and still meet the required mixing efficiencies. When 99.9% of the produced water has been removed, the remaining 0.1% consists of thousands of very small droplets more or less evenly distributed throughout the oil. To contact them would require either a large amount of dilution water dispersed in the oil or a somewhat smaller amount with better droplet dispersion. Whatever the required amount, it can be attained without exceeding the dilution water rates shown in the earlier example.

Water contained in each desalter unit is an excellent source of volume ratio makeup through the use of a recycle option (Figure 7.6). The amount of water recycled to the first stage must be the same as the dilution water injection rate to maintain the water level in the second-stage unit. The volume of water recycled to the second-stage inlet can be any amount, since it immediately rejoins the controlled water volume in the lower portion of the desalter unit (internal recycle). An additional pump may be used (Figure 7.6) for recycling first-stage water to first-stage inlet. The first-stage internal recycle is not necessarily required for each installation and is dependent upon amount of produced water present in the inlet stream. In terms of water requirements, internal recycle may be ignored since it does not add salt or water volume to the stream process.

Emulsions may also be broken by addition of treating agents, such as soaps, fatty acids, sulfonates, and long-chain alcohols. When a chemical is used for emulsion breaking during desalting, it

![Figure 7.3](image-url)
TABLE 7.2
Calculation for Required Amount of Dilution Water for a Single-Stage Process

\[ Z = BK_1 \]

\[ K_1 = \frac{AK_1 + YK_2E}{A + YE} \]

where

\[ A = \frac{1000X_1}{1 - X_1} \] water in inlet stream, bbl

\[ B = \frac{1000X_2}{1 - X_2} \] water in clean oil, bbl

\[ C = A + Y = \text{water to desalter inlet, bbl} \]

\[ Y \] is the injection water (varies with each problem), bbl

\[ V = A + Y - B = \text{water to disposal, bbl} \]

\[ E \] is the mixing efficiency of \( Y \) with \( A \) (as a function); assume 80%

\[ K_1 \] is the salt per barrel of water in produced oil stream, lb

\[ K_2 \] is the salt per barrel of dilution water, lb

\[ K_3 = \frac{AK_1 + YK_2E}{A + YE} \] which is the salt per barrel of water to desalter inlet, lb

\[ X_1 \] is the fraction of water in produced oil stream

\[ X_2 \] is the fraction of water in clean oil outlet

\[ Z \] is the salt in outlet clean oil per 1000 bbl of net oil, lb

\[ a \] See Figure 7.4.

FIGURE 7.4 A single-stage desalting system.

may be added at one or more of three points in the system. First, it may be added to the crude oil before it is mixed with freshwater. Second, it may be added to the freshwater before mixing with the crude oil. Third, it may be added to the mixture of crude oil and water. A high-potential field across the settling vessel also aids coalescence and breaks emulsions, in which case dissolved salts and impurities are removed with the water.
Pretreatment and Distillation

If the oil entering the desalter is not hot enough, it may be too viscous to permit proper mixing and complete separation of the water and the oil, and some of the water may be carried into the fractionator. If, on the other hand, the oil is too hot, some vaporization may occur, and the resulting turbulence can result in improper separation of oil and water. The desalter temperature is therefore quite critical, and normally a bypass is provided around at least one of the exchangers so that the temperature can be controlled. The optimum temperature depends upon the desalter pressure and the quantity of light material in the crude, but is normally approximately 120°C (250°F), 100°C (212°F), being lower for low pressures and light crude oils. The average water injection rate is 5% of the charge. Regular laboratory analyses will monitor the desalter performance, and the desalted crude should normally not contain more than one kilogram of salt per 1000 barrels of feed.

It is not always possible to avoid the injection of water into the desalter. In some cases, the water may be necessary to control the pressure. In such cases, the injection must be done in a controlled manner to avoid removing too much water from the system. The injection water should be of lower salinity than the inlet water, and the injection rate should be controlled to maintain the desired water content in the desalted crude. The injection water should be added to the desalter in a controlled manner, and the rate should be adjusted to maintain the desired water content in the desalted crude.

**TABLE 7.3**
Calculation for Required Amount of Dilution Water for a Two-Stage Process

\[
VK_1 = \frac{BAK_1(R - C) + SYK_1(R - E_2C)}{SR + BE_2(C - R)}
\]

\[
V = B + Y - C
\]

\[
Z = BK_2 + YK_1 - VK_1
\]

where

\[
A = \frac{1000X_1}{1 - X_1} = \text{water in inlet stream to facility, bbl}
\]

\[
B = \frac{1000X_2}{1 - X_2} = \text{water in effluent of first stage, bbl}
\]

\[
C = \frac{1000X_3}{1 - X_3} = \text{water in effluent of second-stage desalter, bbl}
\]

Y is the injection water of lower salinity than inlet water (A), bbl

V is the recycle water to injection in first-stage inlet line, bbl

E_1 is the mixing efficiency of V with A (as a fraction), assumed 80%

E_2 is the mixing efficiency of Y with B (as a fraction), assumed 80%

X_1 is the fraction of water in inlet stream to facility

X_2 is the fraction of water in first-stage outlet oil

X_3 is the fraction of water in second-stage outlet oil

K_1 is the salt per barrel of water to facility, lb

K_2 is the salt per barrel of water to first-stage desalter, lb

K_3 is the salt per barrel of water to second-stage desalter, lb

S is the salt in outlet per 1000 bbl of net oil, lb

Note: All water volumes are per 1000 bbl net oil, all salt contents are pounds of total dissolved salts per barrel of water, and Y varies with each individual problem.

\[a\] See Figure 7.5.
chloride content in the overhead receiver water is greater than 30 ppm, then caustic should be injected at the rate of 1–3 lb per 1000 barrels of charge to reduce the chloride content to the range of 10–30 ppm. Salting out will occur below 10 and severe corrosion above 30 ppm. Another controlling factor on the overhead receiver water is pH. This should be controlled between pH 5.5 and 6.5. Ammonia injection into the tower top section can be used as a control for this. In addition to electrical methods...
Pretreatment and Distillation

for desalting, desalting may also be achieved by using the concept of a packed column (Figure 7.2) that facilitates the separation of the crude oil and brine through the agency of an adsorbent.

Finally, flashing the crude oil feed can frequently reduce corrosion in the principal distillation column. In the flashing operation, desalted crude is heat exchanged against other heat sources that are available to recover maximum heat before crude is charged to the heater, which ultimately supplies all the heat required for operation of the atmospheric distillation unit. Having the heater transfer temperature offset, the flow of fuel to the burners allows control of the heat input. The heater transfer temperature is merely a convenient control, and the actual temperature, which has no great significance, will vary from 320°C (610°F) to as high as 430°C (805°F), depending on the type of crude oil and the pressure at the bottom of the fractionating tower.

7.3 DISTILLATION

Distillation has remained a major refinery process and a process to which crude oil that enters the refinery is subjected. In early refineries, distillation was the primary means by which products were separated from crude petroleum. As the technologies for refining evolved into the twentieth century, refineries became much more complex but distillation remained the prime means by which petroleum is refined. Indeed, the distillation section of a modern refinery is the most flexible unit in the refinery since conditions can be adjusted to process a wide range of refinery feedstocks from the lighter crude oils to the heavier, more viscous crude oils. Generally, the maximum permissible temperature (in the vaporizing furnace or heater) to which the feedstock can be subjected is 350°C (660°F). The rate of thermal decomposition increases markedly above this temperature, although higher temperatures (up to approximately 395°C, 745°F) are part of the specifications for some distillation units—serious cracking does not occur at these higher temperatures but is subject to the properties of the crude oil feedstock and the residence time of the feedstock in the hot zone. If unplanned cracking occurs within a distillation unit, coke deposition can occur in the heater pipes or in the tower itself, resulting in failure of the distillation unit.

Generally, the maximum permissible temperature of the feedstock in the vaporizing furnace is the factor limiting the range of products in a single-stage (atmospheric) column. Thermal decomposition or cracking of the constituents begins as the temperature of the oil approaches 350°C (660°F), and the rate increases markedly above this temperature. However, the decomposition is time dependent, and temperatures on the order of 395°C (745°F) may be employed provided the residence time of the feedstocks in the hot zone does not cause thermal decomposition of the constituents. Thermal decomposition is generally regarded as being undesirable because the coke-like material produced tends to be deposited on the tubes with consequent formation of hot spots and eventual failure of the affected tubes. In the processing of lubricating oil stocks, an equally important consideration in the avoidance of these high temperatures is the deleterious effect on the lubricating properties. However, there are occasions when cracking distillation might be regarded as beneficial and the still temperature will be adjusted accordingly. In such a case, the products will be named accordingly using the prefix cracked, for example, cracked residuum in which case the term pitch (Chapter 1) is applied.

Based upon chemical characteristics, a very approximate estimation of the potential for thermal decomposition of various feedstocks can be made using the Watson characterization factor (Speight, 2014a), \( K_w \):

\[
k_w = \frac{T_b^{1/3}}{\text{sp gr}}
\]

where

- \( T_b \) is the mean average boiling point in degrees Rankine (\( ^\circ\text{R} = ^\circ\text{F} + 459.67 \))
- \( \text{sp gr} \) is the specific gravity
The characterization factor ranges from approximately 10 for paraffinic crude oil to approximately 15 for highly aromatic crude oil. On the assumption that the components of paraffinic crude oil are more thermally labile than the components of aromatic crude oil, it might be supposed that a relationship between the characterization factor and temperature is viable. However, the relationship is so broad that it may not be sufficiently accurate to help the refiner. There are occasions when cracking distillation might be regarded as beneficial and the still temperature will be adjusted accordingly. In such a case, the products will be named accordingly using the prefix cracked, for example, cracked residuum in which case the arbitrary term pitch is applied.

In the modern sense, distillation was the first method by which petroleum was refined (Speight, 2014a). As petroleum refining evolved, distillation became a formidable means by which various products were separated. Further evolution saw the development of topping or skimming or hydroskimming refineries (Figure 7.7) and conversion refineries (Figure 7.8) named for the manner in which petroleum was treated in each case. And many of these configurations exist in the world of modern refining. However, of all the units in a refinery, the distillation section comprising the atmospheric unit and the vacuum unit is required to have the greatest flexibility in terms of variable quality of feedstock and range of product yields. This flexibility is somewhat reduced because of the tendency to omit the distillation section when heavy oil, extra heavy oils, and tar sand bitumen enter the refinery. Thus, refinery configurations can be adapted to the properties of the feedstocks that may dictate no distillation or a simple removal of any volatile constituents.

The simplest refinery configuration, called a topping refinery, is designed to remove volatile constituents from a feedstock under simple conditions. 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 (Figure 7.7), which can also produce desulfurized distillate fuels and high octane gasoline.

![FIGURE 7.7 A hydroskimming refinery (see also Figure 7.8).](image-url)
The most versatile refinery configuration today is known as the conversion refinery (Figure 7.8). 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 unleaded gasoline, with the balance distributed between high-quality jet fuel, liquefied petroleum gas (LPG), low-sulfur 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.

A multitude of separations are accomplished by distillation, but its most important and primary function in the refinery is its use of the distillation tower and the temperature gradients therein (Figure 7.9) for the separation of crude oil into fractions that consists of varying amounts of different components (Table 7.4; Figure 7.10) (Speight, 2000, 2014a). Thus, it is possible to obtain products ranging from gaseous materials taken off the top of the distillation column to a nonvolatile atmospheric residuum (atmospheric bottoms, reduced crude) with correspondingly lower-boiling materials (gas, gasoline, naphtha, kerosene, and gas oil) taken off at intermediate points with each crude oil providing different amounts of the various fractions (Figure 7.11) (Diwekar, 1995; Jones, 1995; Speight, 2000, 2014a; Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007).

The reduced crude may then be processed by vacuum or steam distillation to separate the high-boiling lubricating oil fractions without the danger of decomposition, which occurs at high (>350°C, 660°F) temperatures (Speight, 2000, 2014a). Indeed, atmospheric distillation may be terminated with a lower-boiling fraction (boiling cut) if it is thought that vacuum or steam distillation will yield a better-quality product or if the process appears to be economically more favorable.
It should be noted at this point that not all crude oils yield the same distillation products because of the differences in composition (Charbonnier et al., 1969; Coleman et al., 1978; Speight, 2012). In fact, the nature of the crude oil dictates the processes that may be required for refining. Petroleum can be classified according to the nature of the distillation residue, which in turn depends on the relative content of hydrocarbon types: paraffins, naphthenes, and aromatics. For example, a paraffin-base crude oil produces distillation cuts with higher proportions of paraffins than asphalt.

### Table 7.4

**Boiling Fractions of Petroleum**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>°F</td>
</tr>
<tr>
<td>Fuel gas</td>
<td>−160 to −40</td>
<td>−260 to −40</td>
</tr>
<tr>
<td>Propane</td>
<td>−40</td>
<td>−40</td>
</tr>
<tr>
<td>Butane(s)</td>
<td>−12 to −1</td>
<td>11 to 30</td>
</tr>
<tr>
<td>Light naphtha</td>
<td>−1 to 150</td>
<td>30 to 300</td>
</tr>
<tr>
<td>Heavy naphtha</td>
<td>150 to 205</td>
<td>300 to 400</td>
</tr>
<tr>
<td>Gasoline</td>
<td>−1 to 180</td>
<td>30 to 355</td>
</tr>
<tr>
<td>Kerosene</td>
<td>205 to 260</td>
<td>400 to 500</td>
</tr>
<tr>
<td>Stove oil</td>
<td>205 to 290</td>
<td>400 to 550</td>
</tr>
<tr>
<td>Light gas oil</td>
<td>260 to 315</td>
<td>500 to 600</td>
</tr>
<tr>
<td>Heavy gas oil</td>
<td>315 to 425</td>
<td>600 to 800</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>&gt;400</td>
<td>&gt;750</td>
</tr>
<tr>
<td>Vacuum gas oil</td>
<td>425 to 600</td>
<td>800 to 1100</td>
</tr>
<tr>
<td>Residuum</td>
<td>&gt;600</td>
<td>&gt;1100</td>
</tr>
</tbody>
</table>
FIGURE 7.10  Variation of distillate composition with boiling range.

FIGURE 7.11  Distillation fractionation of different feedstocks.
base crude. The converse is also true; that is, an asphalt-base crude oil produces materials with higher proportions of cyclic compounds. A paraffin-base crude oil yields wax distillates rather than the lubricating distillates produced by the naphthenic-base crude oils. The residuum from paraffin-base petroleum is referred to as “cylinder stock” rather than “asphaltic bottoms,” which is the name often given to the residuum from distillation of naphthenic crude oil. It is emphasized that, in these cases, it is not a matter of the use of archaic terminology but a reflection of the nature of the product and the petroleum from which it is derived.

### 7.3.1 Distillation at Atmospheric Pressure

Distillation columns are the most commonly used separation units in a refinery. Operation is based on the difference in boiling temperatures of the liquid mixture components, and on recycling countercurrent gas–liquid flow. The properly organized temperature distribution up the column results in different mixture compositions at different heights. While multicomponent interphase mass transfer is a common phenomenon for all column types, the flow regimes are very different depending on the internal elements used. The two main types are a tray column and a packed column, the latter equipped with either random or structured packing. Different types of distillation columns are used for different processes, depending on the desired liquid holdup, capacity (flow rates), and pressure drop but each column is a complex unit, combining many structural elements.

The present-day petroleum distillation unit is, in fact, a collection of distillation units that enable a fairly efficient degree of fractionation to be achieved. In contrast to the early units, which consisted of separate stills, a tower is used in the modern-day refinery. In fact, of all the units in a refinery, the distillation unit (Figure 7.12) is required to have the greatest flexibility in terms of variable

![Distillation Diagram](image-url)
quality of feedstock and range of product yields. Thus, crude oil can be separated into gasoline, kerosene, diesel oil, gas oil, and other products, by distillation at atmospheric pressure. Distillation is an operation in which vapors rising through fractionating decks in a tower are intimately contacted with liquid descending across the decks so that higher-boiling components are condensed, and concentrate at the bottom of the tower while the lighter ones are concentrated at the top or pass overhead.

It is common practice to use furnaces to heat the feedstock only when distillation temperatures above 205°C (400°F) are required. Lower temperatures (such as that used in the redistillation of naphtha and similar low-boiling products) are provided by heat exchangers and/or steam reboilers. Thus, the desalted feedstock is generally pumped to the unit directly from a storage tank, and it is important that charge tanks be drained completely free from water before charging to the unit. The crude feedstock is heat exchanged against whatever other heat sources are available to recover maximum heat before crude is charged to the heater, which ultimately supplies all the heat required for operation of the distillation unit.

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

Pipe still furnaces vary greatly in size, shape, and interior arrangement and can accommodate 25,000 bbl or more of crude petroleum per day. The walls and ceiling are insulated with firebrick, and gas or oil burners are inserted through one or more walls. 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 into which the burners discharge and where the oil reaches its highest temperature.

Heat exchangers are also used to preheat the feedstock before it enters the furnace. These exchangers are bundles of tubes arranged within a shell so that a stream passes through the tubes in the opposite direction of a stream passing through the shell. Thus, cold crude oil, by passing through a series of heat exchangers where hot products from the distillation tower are cooled, before entering the furnace and saving of heat in this manner, may be a major factor in the economical operation of refineries.

Steam reboilers may take the form of a steam coil in the bottom of the fractional distillation tower or in a separate vessel. In the latter case, the bottom product from the tower enters the reboiler where part is vaporized by heat from the steam coil. The hot vapor is directed back to the bottom of the tower and provides part of the heat needed to operate the tower. The nonvolatile product leaves the reboiler and passes through a heat exchanger, where its heat is transferred to the feed to the tower. Steam may also be injected into a fractional distillation tower not only to provide heat but also to induce boiling to take place at lower temperatures. Reboilers generally increase the efficiency of fractionation, but a satisfactory degree of separation can usually be achieved more conveniently by the use of a stripping section. The stripping operation occurs in that part of the tower below the point at which the feed is introduced. The more volatile components are stripped from the descending liquid. Above the feed point (the rectifying section), the concentration of the less volatile component in the vapor is reduced.

If water is entrained in the charge, it will vaporize in the exchangers and in the heater, and cause a high-pressure drop through that equipment. If a slug of water should be charged to the unit, the quantity of steam generated by its vaporization is so much greater than the quantity of vapor obtained from the same volume of oil, that the decks in the fractionating column could be
damaged. Water expands in volume 1600 times upon vaporization at 100°C (212°F) at atmospheric pressure.

The feed to a fractional distillation tower is heated by flow through pipe arranged within a large furnace. The heating unit is known as a pipe still heater or pipe still furnace, and the heating unit and the fractional distillation tower make up the essential parts of a distillation unit or pipe still (Figure 7.12). The pipe still furnace heats the feed to a predetermined temperature, usually a temperature at which a calculated portion of the feed changes into vapor. The vapor is held under pressure in the pipe still furnace until it discharges as a foaming stream into the fractional distillation tower. Here the vapors pass up the tower to be fractionated into gas oil, kerosene, and naphtha, while the nonvolatile or liquid portion of the feed descends to the bottom of the tower to be pumped away as a bottom product.

Heat exchangers are used to preheat the crude oil feedstock before entry into the distillation unit. In order to reduce the cost of operating a crude unit, as much heat as possible is recovered from the hot streams by heat exchanging them with the cold crude charge. The number of heat exchangers within the crude unit and cross heat exchange with other units will vary with unit design. A record should be kept of heat exchanger outlet temperatures so that fouling can be detected and possibly corrected before the capacity of the unit is affected.

Crude entering the flash zone of the fractionating column flashes into the vapor that rises up the column and the liquid residue that drops downward. This flash is a very rough separation; the vapors contain appreciable quantities of heavy ends, which must be rejected downward into reduced crude, while the liquid contains lighter products, which must be stripped out. In the distillation of crude petroleum, light naphtha and gases are removed as vapor from the top of the tower, heavy naphtha, kerosene, and gas oil are removed as sidestream products and reduced crude is taken from the bottom of the tower.

Having the heater transfer temperature reset, flow of fuel to the burners controls the heat input. The heater transfer temperature is merely a convenient control, and the actual temperature, which has no great significance, will vary from 320°C (610°F) to as high as 430°C (805°F), depending on the type of crude and the pressure at the bottom of the fractionating tower. It is noteworthy that if the quantity of gasoline and kerosene in a crude is reduced, the transfer temperature required for the same operation will be increased, even though the lift is less. However, at such temperatures, the residence time of the crude oil and its fractions exerts considerable influence on the potential for racking reactions to occur. This is particularly important in determining the properties of the atmospheric residuum.

External reflux that is returned to the top of the fractionator passes downward against the rising vapors. Lighter components of the reflux are vaporized and return to the top of the column while the heavier components in the rising vapors are condensed and return down the column. Thus, there is an internal reflux stream flowing from the top of the fractionator all the way back to the flash zone and becoming progressively heavier as it descends.

The products heavier than the net overhead are obtained by withdrawing portions of the internal reflux stream. The end point of a sidestream fraction (side cut) will depend on the quantity withdrawn. If the sidestream fraction withdrawal rate is increased, the extra product is material that was formerly flowing down the fractionator as internal reflux. Since the internal reflux below the drawoff is reduced, heavier vapors can now rise to that point and result in a heavier product. Changing the drawoff rate is the manner in which sidestream fractions are kept on end point specifications. The temperature of the drawoff decks is an indication of the end point of the product drawn at that point and the drawoff rate can be controlled to hold a constant deck temperature and therefore a specification product.

The degree of fractionation is generally judged by measuring the number of degrees centigrade between the 95% point of the lighter product and the 5% point of the heavier product. The initial boiling point (IBP) and the final boiling point (FBP) can be used but the initial boiling point varies
Pretreatment and Distillation

with the intensity of efficiency of the stripping operation. Fractionation can be improved by increasing the reflux in the fractionator, which is done by raising the transfer temperature. There may be occasions when the internal reflux necessary to achieve satisfactory fractionation between the heavier products is so great that if it was supplied from the top of the fractionator the upper decks will flood. An *intermediate circulating reflux* (ICR) solves this problem. Some internal reflux is withdrawn, pumped through a cooler, or exchanger, and returned colder a few decks higher in the column. This cold oil return condenses extra vapors to liquid and increases the internal reflux below that point. Improvement in the fractionation between the light and heavy gas oil can be achieved by increasing the heater transfer temperature, which would cause the top reflux to increase and then restore the top reflux to its former rate by increasing the circulating reflux rate. Even though the heater transfer temperature is increased, the extra heat is recovered by exchange with crude oil feedstock and, as a result, the heater duty will only increase slightly.

Sometimes a fractionator will be *pulled dry* insofar as the rate at which a product is being withdrawn is greater than the quantity of internal reflux in the fractionator. All the internal reflux then flows to the stripper, the decks below the drawoff run dry, and therefore no fractionation takes place, while at the same time there is insufficient material to maintain the level in the stripper, and the product pump will tend to lose suction. It is necessary then to either lower the product withdrawal rate or to increase the internal reflux in the tower by raising the transfer temperature or by reducing the rate at which the next lightest product is being withdrawn.

Pipe still furnaces vary greatly in size, shape, and interior arrangement and can accommodate 25,000 bbl or more of crude petroleum per day. The walls and ceiling are insulated with firebrick, and gas or oil burners are inserted through one or more walls. 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 into which the burners discharge and where the oil reaches its highest temperature.

Steam reboilers may take the form of a steam coil in the bottom of the fractional distillation tower or in a separate vessel. In the latter case, the bottom product from the tower enters the reboiler where part is vaporized by heat from the steam coil. The hot vapor is directed back to the bottom of the tower and provides part of the heat needed to operate the tower. The nonvolatile product leaves the reboiler and passes through a heat exchanger, where its heat is transferred to the feed to the tower. Steam may also be injected into a fractional distillation tower not only to provide heat but also to induce boiling to take place at lower temperatures. Reboilers generally increase the efficiency of fractionation, but a satisfactory degree of separation can usually be achieved more conveniently by the use of a *stripping section*.

The *stripping section* is the part of the tower below the point at which the feed is introduced; the more volatile components are stripped from the descending liquid. Above the feed point (the rectifying section), the concentration of the less volatile component in the vapor is reduced. The stripping section is necessary because the flashed residue in the bottom of the fractionator and the sidestream products have been in contact with lighter boiling vapors. These vapors must be removed to meet flash point specifications and to drive the light ends into lighter and (usually) more valuable products.

Steam, usually superheated steam, is used to strip these light ends. Generally, sufficient steam is used to meet a flash point specification and, while a further increase in the quantity of steam may raise the initial boiling point of the product slightly, the only way to substantially increase the initial boiling point of a specific product is to increase the yield of the next lighter product. Provided, of course, the fractionator has enough internal reflux to accomplish an efficient separation of the feedstock constituents.

All of the stripping steam that is condensed in the overhead receiver and must be drained off because refluxing water will upset the balance of activities in the fractionator. If the end point of the overhead product is very low, water may not pass overhead and will accumulate on the upper
decks and cause the tower to flood thereby reducing efficiency and perhaps even shut down the
tower. If the latter occurs, and if distillation is the first (other than desalting) process to which a
crude oil is subjected in a refinery, the economic consequences for the refinery operation can be
substantial.

In simple refineries, cut points can be changed slightly to vary yields and balance products, but
the more common practice is to produce relatively narrow fractions and then process (or blend) to
meet product demand. Since all these primary fractions are equilibrium mixtures, they all contain
some proportion of the lighter constituents characteristic of a lower-boiling fraction and so are
stripped of these constituents, or stabilized, before further processing or storage. Thus, gasoline is
stabilized to a controlled butanes–pentanes content, and the overhead may be passed to superfrac-
tionators, towers with a large number of plates that can produce nearly pure C₁–C₄ hydrocarbons
(methane to butanes, CH₄ to C₄H₁₀)—the successive columns termed deethanizers, depropanizers,
debutanizers, and whichever separation columns are still necessary.

Kerosene and gas oil fractions are obtained as sidestream products from the atmospheric tower
(primary tower), and these are treated in stripping columns (i.e., vessels of a few bubble trays) into
which steam is injected and the volatile overhead from the stripper is returned to the primary tower.
Steam is usually introduced by the stripping section of the primary column to lower the temperature
at which fractionation of the heavier ends of the crude can occur.

The specifications for most petroleum products make it extremely difficult to obtain market-
able material by distillation only. In fact, the purpose of atmospheric distillation is considered the
provision of fractions that serve as feedstocks for intermediate refining operations and for blending.
Generally this is carried out at atmospheric pressure, although light crude oils may be topped at an
elevated pressure and the residue then distilled at atmospheric pressure.

The topping operation differs from normal distillation procedures insofar as the majority of the
heat is directed to the feed stream rather than by reboiling the material in the base of the tower.
In addition, products of volatility intermediate between that of the overhead fractions and bottoms
(residua) are withdrawn as sidestream products. Furthermore, steam is injected into the base of
the column and the sidestream strippers to adjust and control the initial boiling range (or point) of
the fractions. Topped crude oil must always be stripped with steam to elevate the flash point or to
recover the final portions of gas oil. The composition of the topped crude oil is a function of the
temperature of the vaporizer (or flasher).

All products are cooled before being sent to storage. Low-boiling products should be restrained
to temperatures below 60°C (140°F) in order to reduce vapor losses in storage, but the need to store
higher-boiling products below such temperatures is not as acute, unless facile oxidation of the prod-
uct at higher temperatures is possible. If a product is being charged to another unit as feedstock,
there may be an advantage in transmitting the hot product to the unit. However, caution is advised
if a product is leaving a unit at temperatures in excess of 100°C (212°F) if there is any possibility of
it entering a tank with water bottoms. The hot oil could readily boil the water and cause the roof to
detach from the tank, perhaps violently!

7.3.2 DISTILLATION AT A REDUCED PRESSURE

The boiling range of the highest boiling fraction that can be produced at atmospheric pressure is
limited by the temperature at which the residue starts to decompose or crack. If the atmospheric
residuum is required for the manufacture of lubricating oils further fractionation without cracking
may be desirable, and this may be achieved by distillation under vacuum. The residua produced by
distillation under reduced pressure have properties markedly different from the residua produced
by distillation at atmospheric pressure (Table 7.5).

Vacuum distillation as applied to the petroleum refining industry is a technique that has seen
wide use in petroleum refining. Vacuum distillation evolved because of the need to separate the
less volatile products, such as lubricating oils, from the petroleum without subjecting these high-boiling products to cracking conditions. The boiling point of the heaviest cut obtainable at atmospheric pressure is limited by the temperature (ca. 350°C; ca. 660°F) at which the residue starts to decompose or crack, unless cracking distillation is preferred. 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.

In order to maximize the production of gas oil and lighter components from the residuum of an atmospheric distillation unit (reduced crude), the residuum can be further distilled in a vacuum distillation unit (Figure 7.12). Residuum distillation is conducted at a low pressure in order to avoid thermal decomposition or cracking at high temperatures. A stock that boils at 400°C (750°F) at 0.1 psi (50 mm) would not boil until approximately 500°C (930°F) at atmospheric pressure and petroleum constituents commence thermal decomposition (cracking) at approximately 350°C (660°F) (Speight, 2000, 2014a). In the vacuum unit, almost no attempt is made to fractionate the products. It is only desired to vaporize the gas oil, remove the entrained residuum, and condense the liquid product as efficiently as possible. Vacuum distillation units that produce lubricating oil fractions are completely different in both design and operation.

In the vacuum tower, the reduced crude is charged through a heater into the vacuum column in the same manner as whole crude is charged to an atmospheric distillation unit (Figure 7.12). Residuum distillation is conducted at a low pressure in order to avoid thermal decomposition or cracking at high temperatures. A stock that boils at 400°C (750°F) at 0.1 psi (50 mm) would not boil until approximately 500°C (930°F) at atmospheric pressure and petroleum constituents commence thermal decomposition (cracking) at approximately 350°C (660°F) (Speight, 2000, 2014a). In the vacuum unit, almost no attempt is made to fractionate the products. It is only desired to vaporize the gas oil, remove the entrained residuum, and condense the liquid product as efficiently as possible. Vacuum distillation units that produce lubricating oil fractions are completely different in both design and operation.

In the vacuum tower, the reduced crude is charged through a heater into the vacuum column in the same manner as whole crude is charged to an atmospheric distillation unit (Figure 7.12). Residuum distillation is conducted at a low pressure in order to avoid thermal decomposition or cracking at high temperatures. A stock that boils at 400°C (750°F) at 0.1 psi (50 mm) would not boil until approximately 500°C (930°F) at atmospheric pressure and petroleum constituents commence thermal decomposition (cracking) at approximately 350°C (660°F) (Speight, 2000, 2014a). In the vacuum unit, almost no attempt is made to fractionate the products. It is only desired to vaporize the gas oil, remove the entrained residuum, and condense the liquid product as efficiently as possible. Vacuum distillation units that produce lubricating oil fractions are completely different in both design and operation.

### TABLE 7.5
Properties of Atmospheric (b.p. >650°F) and Vacuum Residua (b.p. >1050°F)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Gravity API</th>
<th>Sulfur wt%</th>
<th>Nitrogen wt%</th>
<th>Nickel ppm</th>
<th>Vanadium ppm</th>
<th>Asphaltenes (Heptane) wt%</th>
<th>Carbon Residue (Conradson) wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabian light &gt;650°F</td>
<td>17.7</td>
<td>3.0</td>
<td>0.2</td>
<td>10.0</td>
<td>26.0</td>
<td>1.8</td>
<td>7.5</td>
</tr>
<tr>
<td>Arabian light &gt;1050°F</td>
<td>8.5</td>
<td>4.4</td>
<td>0.5</td>
<td>24.0</td>
<td>66.0</td>
<td>4.3</td>
<td>14.2</td>
</tr>
<tr>
<td>Arabian heavy &gt;650°F</td>
<td>11.9</td>
<td>4.4</td>
<td>0.3</td>
<td>27.0</td>
<td>103.0</td>
<td>8.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Arabian heavy &gt;1050°F</td>
<td>7.3</td>
<td>5.1</td>
<td>0.3</td>
<td>40.0</td>
<td>174.0</td>
<td>10.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Alaska North Slope &gt;650°F</td>
<td>15.2</td>
<td>1.6</td>
<td>0.4</td>
<td>18.0</td>
<td>30.0</td>
<td>2.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Alaska North Slope &gt;1050°F</td>
<td>8.2</td>
<td>2.2</td>
<td>0.6</td>
<td>47.0</td>
<td>82.0</td>
<td>4.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Lloydminster (Canada) &gt;650°F</td>
<td>10.3</td>
<td>4.1</td>
<td>0.3</td>
<td>65.0</td>
<td>141.0</td>
<td>14.0</td>
<td>12.1</td>
</tr>
<tr>
<td>Lloydminster (Canada) &gt;1050°F</td>
<td>8.5</td>
<td>4.4</td>
<td>0.6</td>
<td>115.0</td>
<td>252.0</td>
<td>18.0</td>
<td>21.4</td>
</tr>
<tr>
<td>Kuwait &gt;650°F</td>
<td>13.9</td>
<td>4.4</td>
<td>0.3</td>
<td>14.0</td>
<td>50.0</td>
<td>2.4</td>
<td>12.2</td>
</tr>
<tr>
<td>Kuwait &gt;1050°F</td>
<td>5.5</td>
<td>5.5</td>
<td>0.4</td>
<td>32.0</td>
<td>102.0</td>
<td>7.1</td>
<td>23.1</td>
</tr>
<tr>
<td>Tia Juana &gt;650°F</td>
<td>17.3</td>
<td>1.8</td>
<td>0.3</td>
<td>25.0</td>
<td>185.0</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>Tia Juana &gt;1050°F</td>
<td>7.1</td>
<td>2.6</td>
<td>0.6</td>
<td>64.0</td>
<td>450.0</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>Taching &gt;650°F</td>
<td>27.3</td>
<td>0.2</td>
<td>0.2</td>
<td>5.0</td>
<td>1.0</td>
<td>4.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Taching &gt;1050°F</td>
<td>21.5</td>
<td>0.3</td>
<td>0.4</td>
<td>9.0</td>
<td>2.0</td>
<td>7.6</td>
<td>7.9</td>
</tr>
</tbody>
</table>
penetration specification for asphalt. The penetration of an asphalt is the depth in 1/100 cm to which a needle carrying a 100 g weight sinks into a sample at 25°C (77°F) in 5 seconds (ASTM D5), so that the lower the penetration, the heavier the residuum or asphalt. If the flash zone temperature is too high the crude can start to crack and produce gases that overload the ejectors and break the vacuum. It is then necessary to lower the temperature and if a heavier residuum product is still required, an attempt should be made to obtain a better vacuum.

Slight cracking may occur without seriously affecting the vacuum, and the occurrence of cracking can be established by a positive result from the Oliensis Spot Test (Speight, 2014a, 2015). This test is a convenient laboratory test that indicates the presence of cracked components as sediment by the separation of the sediment when a 20% solution of asphalt in naphtha is dropped on a filter paper. However, some crude oils yield a residuum that exhibit a positive test for the presence of sediment (solid phase) in the residuum. If a negative test result is required, operation at the highest vacuum and lowest temperature should be attempted. Since the degree of cracking depends on both the temperature and the time (residence time in the hot zone) during which the oil is exposed to that temperature, the level of the residuum in the bottom of the tower should be held at a minimum, and its temperature reduced by recirculating some of the residuum from the outlet of the residuum/crude oil heat exchanger to the bottom of the column. Quite often, when the level of the residuum rises the column vacuum falls because of cracking due to increased residence time.

The flash zone temperature will vary widely and is dependent on the source of the crude oil, residuum specifications, the quantity of product taken overhead, and the flash zone pressure, and temperatures from below 315°C (600°F) to more than 425°C (800°F) have been used in commercial operations. Some vacuum distillation units are provided with facilities to strip the residuum with steam, and this will tend to lower the temperature necessary to meet an asphalt specification, but an excessive quantity of steam will overload the jets.

The distillation of high-boiling lubricating oil stocks may require pressures as low as 0.29–0.58 psi (15–30 mm Hg), but operating conditions are more usually 0.97–1.93 psi (50–100 mm Hg). Volumes of vapor at these pressures are large and pressure drops must be small to maintain control, so vacuum columns are necessarily of large diameter. Differences in vapor pressure of different fractions are relatively larger than for lower-boiling fractions, and relatively few plates are required. Under these conditions, a heavy gas oil may be obtained as an overhead product at temperatures of approximately 150°C (300°F). Lubricating oil fractions may be obtained as sidestream products at temperatures of 250°C–350°C (480°F–660°F). The feedstock and residue temperatures being kept below the temperature of 350°C (660°F), above which the rate of thermal decomposition (cracking) increases (Speight, 2000, 2014a). The partial pressure of the hydrocarbons is effectively reduced yet further by the injection of steam. The steam added to the column, principally for the stripping of bitumen in the base of the column, is superheated in the convection section of the heater.

When trays similar to those used in the atmospheric column are used in vacuum distillation, the column diameter may be extremely high, up to 45 ft (14 m). To maintain low-pressure drops across the trays, the liquid seal must be minimal. The low holdup and the relatively high viscosity of the liquid limit the tray efficiency, which tends to be much lower than in the atmospheric column. The vacuum is maintained in the column by removing the noncondensable gas that enters the column by way of the feed to the column or by leakage of air.

The fractions obtained by vacuum distillation of reduced crude depend on whether the run is designed to produce lubricating or vacuum gas oils. In the former case, the fractions include (1) heavy gas oil, 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) obtained as a sidestream product; and (3) residuum, the nonvolatile product that may be used directly as asphalt or to asphalt. The residuum may also be used as a feedstock for a coking
Pretreatment and Distillation

operation or blended with gas oils to produce a heavy fuel oil. However, if the reduced crude is not required as a source of lubricating oils, the lubricating and heavy gas oil fractions are combined or, more likely, removed from the residuum as one fraction and used as a catalytic cracking feedstock.

Three types of high-vacuum units for long residue upgrading have been developed for commercial application: (1) feedstock preparation units, (2) lube oil high-vacuum units, and (3) high-vacuum units for asphalt production.

The feedstock preparation units make a major contribution to deep conversion upgrading and produce distillate feedstocks for further upgrading in catalytic crackers, hydrocracking units, and coking units. To obtain an optimum waxy distillate quality a wash oil section is installed between feed flash zone and waxy distillate drawoff. The wash oil produced is used as fuel component or recycled to feed. The flashed residue (short residue) is cooled by heat exchange against long residue feed. A slipstream of this cooled short residue is returned to the bottom of the high-vacuum column as quench to minimize cracking (maintain low bottom temperature).

Lube oil high-vacuum units are specifically designed to produce high-quality distillate fractions for lube oil manufacturing. Special precautions are therefore taken to prevent thermal degradation of the distillates produced. The units are of the wet type. Normally, three sharply fractionated distillates are produced (spindle oil, light machine oil, and medium machine oil). Cut points between those fractions are typically controlled on their viscosity quality. Spindle oil and light machine oil are subsequently steam stripped in dedicated strippers. The distillates are further processed to produce lubricating base oil. The short residue is normally used as feedstock for the solvent deasphalted process to produce deasphalted oil, an intermediate for bright stock manufacturing. High-vacuum units for asphalt production are designed to produce straight-run asphalt and/or feedstocks for residuum blowing to produce blown asphalt that meets specifications. In principle, these units are designed on the same basis as feed preparation units, which may also be used to provide feedstocks for asphalt manufacturing.

Deep cut vacuum distillation involving a revamp of the vacuum distillation unit to cut deeper into the residue is one of the first options available to the refiner. In addition to the limits of the major equipment, other constraints include (1) the vacuum gas oil quality specification required by downstream conversion units, (2) the minimum flash zone pressure achievable, and (3) the maximum heater outlet temperature achievable without excessive cracking. These constraints typically limit the cut point (true boiling point) to 560°C–590°C (1040°F–1100°F) although units are designed for cut points (true boiling point) as high as 627°C (1160°F).

Prior to 1960, most of the trays in a vacuum tower were conventional designed to provide as low a pressure drop as possible. Many of these standard trays have been replaced by grid packing that provides very low-pressure drops as well as a high tray efficiency. Up to this time, flash zone temperature reduction was enhanced by steam stripping of the residuum but with the new grid packing the use of steam to enhance flash temperature has been eliminated and most modern units are dry vacuum units.

If the reduced crude is not required as a source of lubricating oils, the lubricating and heavy gas oil fractions are combined or, more likely, removed from the residuum as one fraction and used as a catalytic cracking feedstock. The continued use of atmospheric and vacuum distillation has been a major part of refinery operations during this century and no doubt will continue to be employed, at least into the beginning decades of the twenty-first century, as the primary refining operation.

The vacuum residuum (vacuum bottoms) must be handled more carefully than most refinery products since the pumps that handle hot heavy material have a tendency to lose suction. Recycling cooled residuum to the column bottom thereby reducing the tendency of vapor to form in the suction line can minimize this potential situation. It is also important that the residuum pump be sealed in such a manner so as to prevent the entry of air. In addition, and since most vacuum residua are solid at ambient temperature, all vacuum residua handling equipment must either be kept active, or
flushed out with gas oil, when it is shut down. Steam tracing alone may be inadequate to keep the residuum fluid, but where this is done, the high-pressure steam should be used.

The vacuum residuum from a vacuum tower is sometimes cooled in open box units, as shell-and-tube units are not efficient in this service. It is often desirable to send residuum to storage at high temperature to facilitate blending. If it is desired to increase the temperature of the residuum, it is better to do so by lowering the level of water in the open box and not by lowering the water temperature. If the water in the box is too cold, the residuum can solidify on the inside wall of the tube and insulate the hot residuum in the central core from the cooling water. Lowering the water temperature can actually result in a hotter product. When the residuum is sent to storage at over 100°C (212°F), care should be taken to insure that the tank is absolutely free from water. Residuum coolers should always be flushed out with gas oil immediately once the residuum flow stops, since melting the contents of a cooler is a slow process.

The vapor rising above the flash zone will entrain some residuum that cannot be tolerated in cracking unit charge. The vapor is generally washed with gas oil product, sprayed into the slop wax section. The mixture of gas oil and entrained residuum is known as slop wax, and it is often circulated over the decks to improve contact, although the circulation rate may not be critical. The final stage of entrainment removal is obtained by passing the rising vapors through a metallic mesh demister blanket through which the fresh gas oil is sprayed.

Most of the gas oil spray is vaporized by the hot rising vapors and returned up the column. Some slop wax must be yielded in order to reject the captured entrainment. The amount of spray to the demister blanket is generally varied so that the yield of slop wax necessary to maintain the level in the slop wax pan is approximately 5% of the charge. If the carbon residue or the metals content of the heavy vacuum gas oil is high, a greater percentage of slop wax must be withdrawn or circulated. Variation in the color of the gas oil product is a valuable indication of the effectiveness of entrainment control.

Slop wax is a mixture of gas oil and residuum, and it can be recirculated through the heater to the flash zone and refluxed. If, however, a crude contains volatile metal compounds, these will be recycled with the slop wax and can finally rise into the gas oil. Where volatile metals are a problem, it is necessary either to yield slop wax as a product, or to make lighter asphalt, which will contain the metal compounds returned with the slop wax.

The scrubbed vapor rising above the demister blanket is the product, and no further fractionation is required. It is only desired to condense these vapors as efficiently as possible. This could be done in a shell-and-tube condenser, but these are inefficient at low pressures, and the high-pressure drop through such a condenser would raise the flash zone pressure. The most efficient method is to contact the hot vapors with liquid product that has been cooled by pumping through heat exchangers.

Finally, confusion often arises because of the different scales used to measure the vacuum. Positive pressures are commonly measured as kilograms per square-centimeter gauge, which are kilograms per square centimeter above atmospheric pressure, which is 1.035 kg/cm² or 14.7 psi. Another means of measurement is to measure in millimeters of mercury in which atmospheric pressure (sea level) is 760 mm of mercury absolute while a perfect vacuum is 0 mm absolute.

### 7.3.3 Distillation Towers

Distillation towers (distillation columns) are made up of several components, each of which is used either to transfer heat energy or enhance material transfer. A typical distillation column consists of several major parts: (1) a vertical shell where separation of the components is carried out; (2) column internals such as trays, or plates, or packings that are used to enhance component separation; (3) a reboiler to provide the necessary vaporization for the distillation process; (4) a condenser to cool and condense the vapor leaving the top of the column; and (5) a reflux drum to hold the condensed vapor from the top of the column so that liquid (reflux) can be recycled back to the column. The vertical shell houses the column internals and together with the condenser and reboiler constitutes a distillation column.
In a petroleum distillation unit, the feedstock liquid mixture is introduced usually near the middle of the column to a tray known as the feed tray. The feed tray divides the column into a top (enriching, rectification) section and a bottom (stripping) section. The feed flows down the column where it is collected at the bottom in the reboiler. Heat is supplied to the reboiler to generate vapor. The source of heat input can be any suitable fluid, although in most chemical plants this is normally steam. In refineries, the heating source may be the output streams of other columns. The vapor raised in the reboiler is reintroduced into the unit at the bottom of the column. The liquid removed from the reboiler is known as the bottoms.

The vapor moves up the column, and as it exits the top of the unit, it is cooled by a condenser. The condensed liquid is stored in a holding vessel known as the reflux drum. Some of this liquid is recycled back to the top of the column and this is called the reflux. The condensed liquid that is removed from the system is known as the distillate or top product. Thus, there are internal flows of vapor and liquid within the column as well as external flows of feeds and product streams, into and out of the column.

The tower is divided into a number of horizontal sections by metal trays or plates, and each is the equivalent of a still. The more trays, the more redistillation, and hence the better is the fractionation or separation of the mixture fed into the tower. A tower for fractionating crude petroleum may be 13 ft in diameter and 85 ft high according to a general formula:

\[ c = 220d^2r \]

where
- \( c \) is the capacity in bbl/day
- \( d \) is the diameter in feet
- \( r \) is the amount of residuum expressed as a fraction of the feedstock

A tower stripping unwanted volatile material from gas oil may be only 3 or 4 ft in diameter and 10 ft high with less than 20 trays (Speight, 2014a). Towers concerned with the distillation of liquefied gases are only a few feet in diameter but may be up to 200 ft in height. A tower used in the fractionation of crude petroleum may have from 16 to 28 trays, but one used in the fractionation (superfractionation) of liquefied gases may have 30–100 trays. The feed to a typical tower enters the vaporizing or flash zone, an area without trays. The majority of the trays are usually located above this area. The feed to a bubble tower, however, may be at any point from top to bottom with trays above and below the entry point, depending on the kind of feedstock and the characteristics desired in the products.

### 7.3.3.1 Tray Towers

The tray tower typically combines the open flow channel with weirs, down comers, and heat exchangers. Free surface flow over the tray is disturbed by gas bubbles coming through the perforated tray, and possible leakage of liquid dropping through the upper tray.

Liquid collects on each tray to a depth of, say, several inches and the depth controlled by a dam or weir. As the liquid level rises, excess liquid spills over the weir into a channel (downspout), which carries the liquid to the tray below. The temperature of the trays is progressively cooler from bottom to top. The bottom tray is heated by the incoming heated feedstock, although in some instances a steam coil (reboiler) is used to supply additional heat. As the hot vapors pass upward in the tower, condensation occurs onto the trays until refluxing (simultaneous boiling of a liquid and condensing of the vapor) occurs on the trays. Vapors continue to pass upward through the tower, whereas the liquid on any particular trays spills onto the tray below, and so on until the heat at a particular point is too intense for the material to remain liquid. It then becomes vapor and joins the other vapors passing upward through the tower. The whole tower thus simulates a collection of several (or many) stills, with the composition of the liquid at any one point or on any one tray remaining fairly consistent. This allows part of the refluxing liquid to be tapped off at various points as sidestream products.
The efficient operation of the distillation, or fractionating, tower requires the rising vapors to mix with the liquid on each tray. This is usually achieved by installing a short chimney on each hole in the plate and a cap with a serrated edge (bubble cap, hence bubble-cap tower) over each chimney (Figure 7.13). The cap forces the vapors to go below the surface of the liquid and to bubble up through it. Since the vapors may pass up the tower at substantial velocities, the caps are held in place by bolted steel bars.

Perforated trays are also used in fractionating towers. This tray is similar to the bubble-cap tray but has smaller holes (~3 inches, 6 mm, vs. 2 inches, 50 mm). The liquid spills back to the tray below through weirs and is actually prevented from returning to the tray below through the holes by the velocity of the rising vapors. Needless to say, a minimum vapor velocity is required to prevent return of the liquid through the perforations.

As a result, flashed vapors rise up the fractionating column through the trays and countercurrent to the internal reflux flowing down the column. The lightest product, which is generally gasoline, passes overhead and is condensed in the overhead receiver. If the crude oil contains any noncondensable gas, it will leave the receiver as a gas, and can be recovered by other equipment, which should be operated to obtain the minimum flash zone pressure. The temperature at the top of the fractionator is a good measure of the end point of the gasoline and is controlled by returning some of the condensed gasoline (as reflux) to the top of the column. Increasing the reflux rate lowers the top temperature and results in the net overhead product having a lower end point. The loss in net overhead product must be removed on the next lower draw tray. This decreases the initial boiling point of material from this tray. Increasing the heater transfer temperature increases the heat input and demands more reflux to maintain the same top temperature.

Usually, trays are horizontal, flat, specially prefabricated metal sheets, which are placed at a regular distance in a vertical cylindrical column. Trays have two main parts: (1) the part where vapor (gas) and liquid are being contacted (the contacting area) and (2) the part where vapor and liquid are being separated (the rectifying section and stripping section).
liquid are separated, after having been contacted (the downcomer area). Classification of trays is based on (1) the type of plate used in the contacting area, (2) the type and number of downcomers making up the downcomer area, (3) the direction and path of the liquid flowing across the contacting area of the tray, (4) the vapor (gas) flow direction through the (orifices in) the plate, and (5) the presence of baffles, packing, or other additions to the contacting area to improve the separation performance of the tray.

Common plate types, for use in the contacting area are as follows: (1) bubble cap tray in which caps are mounted over risers fixed on the plate (the caps come in a wide variety of sizes and shapes, round, square, and rectangular [tunnel]); (2) sieve trays that come with different hole shapes (round, square, triangular, rectangular [slots], star), various hole sizes (from approximately 2 mm to approximately 25 mm), and several punch patterns (triangular, square, rectangular); and (3) the valve tray that also is available in a variety of valve shapes (round, square, rectangular, triangular), valve sizes, valve weights (light and heavy), and orifice sizes and is either fixed or floating valves.

Trays usually have one or more downcomers. The type and number of downcomers used mainly depends on the amount of downcomer area required to handle the liquid flow. Single-pass trays are trays with one downcomer delivering the liquid from the next higher tray, a single bubbling area across which the liquid passes to contact the vapor and one downcomer for the liquid to the next lower tray. Trays with multiple downcomers and hence multiple liquid passes can have a number of layout geometries. The downcomers may extend, in parallel, from wall to wall, as in. The downcomers may be rotated 90° (or 180°) on successive trays. The downcomer layout pattern determines the liquid flow path arrangement and liquid flow direction in the contacting area of the trays. Giving a preferential direction to the vapor flowing through the orifices in the plate will induce the liquid to flow in the same direction. In this way, liquid flow rate and flow direction, as well as liquid height, can be manipulated. The presence of baffles, screen mesh or demister mats, loose or restrained dumped packing, and/or the addition of other devices in the contacting area can be beneficial for improving the contacting performance of the tray, namely, its separation efficiency.

The most important parameter of a tray is its separation performance and four parameters are of importance in the design and operation of a tray column: (1) the level of the tray efficiency, in the normal operating range; (2) the vapor rate at the “upper limit,” that is, the maximum vapor load; (3) the vapor rate at the “lower limit,” that is, the minimum vapor load; and (4) the tray pressure drop.

The separation performance of a tray is the basis of the performance of the column as a whole. The primary function of, for instance, a distillation column is the separation of a feed stream in (at least) one top product stream and one bottom product stream. The quality of the separation performed by a column can be judged from the purity of the top and bottom product streams. The specification of the impurity levels in the top and bottom streams and the degree of recovery of pure products set the targets for a successful operation of a distillation column. It is evident that tray efficiency is influenced by (1) the specific component under consideration (this holds specially for multicomponent systems in which the efficiency can be different for each component, because of different diffusivities, diffusion interactions, and different stripping factors) and (2) the vapor flow rate; usually, increasing the flow rate increases the effective mass transfer rate, while it decreases the contact time at the same time. These counteracting effects lead to a roughly constant efficiency value, for a tray in its normal operating range. Upon approaching the lower operating limit a tray starts weeping and loses efficiency.

7.3.3.2 Packed Towers
A packed tower reactor (packed column reactor) is similar to a trickle-bed reactor (Chapter 6), where liquid film flows down over the packing surface in contact with the upward gas flow. A small fragment of packing geometry can be accurately analyzed assuming the periodic boundary conditions, which allows calibration of the porous media model for a big packing segment. The packing in a distillation column creates a surface for the liquid to spread on thereby providing a high surface area for mass transfer between the liquid and the vapor.
Variations in both the atmospheric and vacuum distillation protocols, including the tower internals, are claimed to improve process efficiency and economics. For example, the D2000 process (Figure 7.14) uses progressive distillation to minimize the total energy consumption required for separation. The process is normally applied for new topping units or new integrated topping/vacuum units. Incorporation of a vacuum flasher into the distillation circuit (Figure 7.15) is claimed
to produce an increased yield of distillate materials as well as the usual vacuum residuum. Finally, integration of a crude distillation unit, a hydrodesulfurization unit, a high vacuum unit, and a visbreaker (Figure 7.16) (Chapter 8) also improves efficiency.

In summary, the continued use of atmospheric and vacuum distillation has been a major part of refinery operations during this century and no doubt will continue to be employed, at least into the midpoint and latter decades of the twenty-first century, as the primary refining operation (Speight, 2011).

7.4 OTHER DISTILLATION PROCESSES

Atmospheric distillation and vacuum distillation provide the primary fractions from crude oil to use as feedstocks for other refinery processes for conversion into products. Many of these subsequent processes involve fractional distillation, and some of the procedures are so specialized and used with such frequency that they are identified by name.

7.4.1 STRIPPING

*Stripping* is a fractional distillation operation carried out on each sidestream product immediately after it leaves the main distillation tower. Since perfect separation is not accomplished in the main tower, unwanted components are mixed with those of the sidestream product. The purpose of stripping is to remove the more volatile components and thus reduce the flash point of the sidestream product. Thus, a sidestream product enters at the top tray of a stripper, and as it spills down the four to six trays, steam injected into the bottom of the stripper removes the volatile components. The steam and volatile components leave the top of the stripper to return to the main tower. The stripped sidestream product leaves at the bottom and, after being cooled in a heat exchanger, goes to storage. Since strippers are short, they are arranged one above another in a single tower; each stripper, however, operates as a separate unit.

A tower stripping unwanted volatile material from gas oil may be only 3 or 4 ft in diameter and 10 ft high with less than 20 trays (Table 7.6). Towers concerned with the distillation of liquefied gases are only a few feet in diameter but may be up to 200 ft in height. A tower used in the
fractionation of crude petroleum may have from 16 to 28 trays, but one used in the fractionation
(supercrudefractionation) of liquefied gases may have 30–100 trays. The feed to a typical tower enters the
vaporizing or flash zone, an area without trays. The majority of the trays are usually located above
this area. The feed to a bubble tower, however, may be at any point from top to bottom with trays
above and below the entry point, depending on the kind of feedstock and the characteristics desired
in the products.

7.4.2 Rerunning

Rerunning is a general term covering the redistillation of any material and indicating, usually, that
a large part of the material is distilled overhead. Stripping, in contrast, removes only a relatively
small amount of material as an overhead product. A rerun tower may be associated with a crude
distillation unit that produces wide boiling range naphtha as an overhead product. By separating
the wide-cut fraction into a light and heavy naphtha, the rerun tower acts in effect as an extension of the
crude distillation tower.

The product from chemical treating process of various fractions may be rerun to remove the
treating chemical or its reaction products. If the volume of material being processed is small, a
shell still may be used instead of a continuous fractional distillation unit. The same applies to gas oils and
other fractions from which the front end or tail must be removed for special purposes.

7.4.3 Stabilization

The gaseous and more volatile liquid hydrocarbons produced in a refinery are collectively known as light hydrocarbons or light ends (Table 7.7). Light ends are produced in relatively small quantities from crude petroleum and in large quantities when gasoline is manufactured by cracking and
reforming. When a naphtha or gasoline component at the time of its manufacture is passed through
a condenser, most of the light ends do not condense and are withdrawn and handled as a gas. A
considerable part of the light ends, however, can remain dissolved in the condensate, thus forming a
liquid with a high vapor pressure, which may be categorized as unstable and stabilization is required
(Abdel-Aal et al., 2016).

Liquids with high vapor pressures may be stored in refrigerated tanks or in tanks capable of
withstanding the pressures developed by the gases dissolved in the liquid. The more usual procedure,
however, is to separate the light ends from the liquid by a distillation process generally known as stabilization. Enough of the light ends are removed to make a stabilized liquid, that is, a liquid
with a low enough vapor pressure to permit its storage in ordinary tanks without loss of vapor.
The simplest stabilization process is a stripping process. Light naphtha from a crude tower, for
example, may be pumped into the top of a tall, small-diameter fractional distillation tower operated
under a pressure of 50–80 psi. Heat is introduced at the bottom of the tower by a steam reboiler.
As the naphtha cascades down the tower, the light ends separate and pass up the tower to leave as

<table>
<thead>
<tr>
<th>Degree of Rectification</th>
<th>No. of Trays</th>
<th>Ratio of Vapor to Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stripping still</td>
<td>10–20</td>
<td>Vapor = 20% of feed</td>
</tr>
<tr>
<td>Primary fractionator</td>
<td>20–40</td>
<td>Vapor = 35%–40% of feed</td>
</tr>
<tr>
<td>Secondary fractionator</td>
<td>40–50</td>
<td>Feed = 50% of vapor</td>
</tr>
<tr>
<td>Splitter</td>
<td>50–70</td>
<td>Feed = 25% of vapor</td>
</tr>
<tr>
<td>Superfractionator</td>
<td>70–100</td>
<td>Feed = 10% of vapor</td>
</tr>
</tbody>
</table>

TABLE 7.7
Number of Required Trays According to Tower Function
an overhead product. Since reflux is not used, considerable amounts of liquid hydrocarbons pass overhead with the light ends.

Stabilization is usually a more precise operation than that just described. An example of more precise stabilization can be seen in the handling of the mixture of hydrocarbons produced by cracking. The overhead from the atmospheric distillation tower that fractionates the cracked mixture consists of light ends and cracked gasoline with light ends dissolved in it. If the latter is pumped to the usual type of tank storage, the dissolved gases cause the gasoline to boil, with consequent loss of the gases and some of the liquid components. To prevent this, the gasoline and the gases dissolved in it are pumped to a stabilizer maintained under a pressure of approximately 100 psi and operated with reflux. This fractionating tower makes a cut between the highest boiling gaseous component (butane) and the lowest boiling liquid component (pentane). The bottom product is thus a liquid free of all gaseous components, including butane; hence the fractionating tower is known as a *debutanizer* (Figure 7.17).

The debutanizer bottoms (gasoline constituents) can be safely stored, whereas the overhead from the debutanizer contains the butane, propane ethane, and methane fractions. The butane fraction, which consists of all the hydrocarbons containing four carbon atoms, is particularly needed to give easy starting characteristics to gasoline. It must be separated from the other gases and blended with gasoline in amounts that vary with the season: more in the winter and less in the summer. Separation of the butane fraction is effected by another distillation in a fractional distillation tower called a *depropanizer*, since its purpose is to separate propane and the lighter gases from the butane fraction.

The depropanizer is very similar to the debutanizer, except that it is smaller in diameter because of the smaller volume being distilled and is taller because of the larger number of trays required to make a sharp cut between the butane and propane fractions. Since the normally gaseous propane must exist as a liquid in the tower, a pressure of 200 psi is maintained. The bottom product, known as the butane fraction, stabilizer bottoms, or refinery casinghead, is a high-vapor-pressure material that must be stored in refrigerated tanks or pressure tanks. The depropanizer overhead, consisting of

---

**TABLE 7.7**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Carbon Atoms</th>
<th>Boiling Range</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>16, −182, −296</td>
<td>Fuel gas</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>30, −89, −128</td>
<td>Fuel gas</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2</td>
<td>28, −104, −155</td>
<td>Fuel gas, petrochemicals</td>
</tr>
<tr>
<td>Propane</td>
<td>3</td>
<td>44, −42, −44</td>
<td>Fuel gas, LPG</td>
</tr>
<tr>
<td>Propylene</td>
<td>3</td>
<td>42, −48, −54</td>
<td>Fuel gas, petrochemicals, polymer gasoline</td>
</tr>
<tr>
<td>Iso-Butane</td>
<td>4</td>
<td>58, −12, 11</td>
<td>Alkylate, motor gasoline</td>
</tr>
<tr>
<td>n-Butane</td>
<td>4</td>
<td>58, −1, 31</td>
<td>Automotive gasoline</td>
</tr>
<tr>
<td>Iso-Butylene</td>
<td>4</td>
<td>56, −7, 20</td>
<td>Synthetic rubber and chemicals, polymer gasoline, alkylate, motor gasoline</td>
</tr>
<tr>
<td>Butylene-1*</td>
<td>4</td>
<td>56, −6, 21</td>
<td>Synthetic rubber and chemicals,</td>
</tr>
<tr>
<td>Butylene-2*</td>
<td>4</td>
<td>56, −6, 34</td>
<td>alkylate, gasoline, motor gasoline</td>
</tr>
<tr>
<td>Iso-Pentane</td>
<td>5</td>
<td>72, 28, 82</td>
<td>Automotive and aviation gasolines</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>5</td>
<td>72, 36, 97</td>
<td>Automotive and aviation gasolines</td>
</tr>
<tr>
<td>Pentylene</td>
<td>5</td>
<td>70, 30, 86</td>
<td>Automotive and aviation gasolines</td>
</tr>
<tr>
<td>Iso-Hexane</td>
<td>6</td>
<td>86, 61, 141</td>
<td>Automotive and aviation gasolines</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>6</td>
<td>86, 69, 156</td>
<td>Automotive and aviation gasolines</td>
</tr>
</tbody>
</table>

* Numbers refer to the positions of the double bond. For example, butylene-1 (or butene-1 or but-1-ene) is CH₃CH=CHCH₃, and butylene-2 (or butene-2 or but-2-ene) is CH₃CH=CHCH₃.
propane and lighter gases, is used as a petrochemical feedstock or as a refinery fuel gas, depending on the composition.

A depentanizer is a fractional distillation tower that removes the pentane fraction from a debutanized (butane-free) fraction. Depentanizers are similar to debutanizers and have been introduced recently to segregate the pentane fractions from cracked gasoline and reformate. The pentane fraction when added to a premium gasoline makes this gasoline extraordinarily responsive to the demands of an engine accelerator.

The gases produced as overhead products from crude distillation, stabilization, and depropanization units may be delivered to a gas absorption plant for the recovery of small amounts of butane and higher-boiling hydrocarbons. The gas absorption plant consists essentially of two towers. One tower is the absorber where the butane and higher-boiling hydrocarbons are removed from the lighter gases.

The gas mixture enters at the bottom of the tower and rises to the top. As it does this, it contacts the lean oil, which absorbs the butane and higher-boiling hydrocarbons but not the lower-boiling hydrocarbons. The latter leave the top of the absorber as dry gas. The lean oil that has become enriched with butane and higher-boiling hydrocarbons is now termed *fat oil*. This is pumped from the bottom of the absorber into the second tower, where fractional distillation separates the butane and higher-boiling hydrocarbons as an overhead fraction and the oil, once again lean oil, as the bottom product.

The condensed butane and higher-boiling hydrocarbons are included with the refinery *casing-head bottoms* or *stabilizer bottoms*. The dry gas is frequently used as fuel gas for refinery furnaces. It contains propane and propylene, however, which may be required for liquefied petroleum gas for the manufacture of polymer gasoline or petrochemicals. Separation of the propane fraction (propane and propylene) from the lighter gases is accomplished by further distillation in a fractional distillation tower similar to those previously described and particularly designed to handle liquefied gases. Further separation of hydrocarbon gases is required for petrochemical manufacture.
7.4.4 Superfractionation

The term superfractionation is sometimes applied to a highly efficient fractionating tower used to separate ordinary petroleum products. For example, to increase the yield of furnace fuel oil, heavy naphtha may be redistilled in a tower that is capable of making a better separation of the naphtha and the fuel oil components. The latter, obtained as a bottom product, is diverted to furnace fuel oil.

Fractional distillation as normally carried out in a refinery does not completely separate one petroleum fraction from another. One product overlaps another, depending on the efficiency of the fractionation, which in turn depends on the number of trays in the tower, the amount of reflux used, and the rate of distillation. Kerosene, for example, normally contains a small percentage of hydrocarbons that (according to their boiling points) belong in the naphtha fraction and a small percentage that should be in the gas oil fraction. Complete separation is not required for the ordinary uses of these materials, but certain materials, such as solvents for particular purposes (hexane, heptane, and aromatics), are required as essentially pure compounds. Since they occur in mixtures of hydrocarbons they must be separated by distillation, with no overlap of one hydrocarbon with another. This requires highly efficient fractional distillation towers that are especially designed for this purpose and referred to as superfractionators. Several towers with 50–100 trays operating at high reflux ratios may be required to separate a single compound with the necessary purity.

7.4.5 Azeotropic Distillation

Azeotropic distillation is the use of a third component to separate two close-boiling components by means of the formation of an azeotropic mixture between one of the original components and the third component to increase the difference in the boiling points and facilitates separation by distillation.

Sometimes the separation of a desired compound calls for azeotropic distillation. All compounds have definite boiling temperatures, but a mixture of chemically dissimilar compounds sometimes causes one or both of the components to boil at a temperature other than that expected. The separation of these components of similar volatility may become economical 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 criterion that severely limits the application of extractive and azeotropic distillation. The majority of successful processes, in fact, 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 10°C–40°C (18°F–72°F) below that of the components. Thus, although the entrainer is more volatile than the components and distills off in the overhead product, it is present in a sufficiently high concentration in the rectification section of the column.

The five methods for separating azeotropic mixtures are as follows: (1) homogeneous azeotropic distillation where the liquid separating agent is completely miscible; (2) heterogeneous azeotropic distillation, or more commonly, azeotropic distillation where the liquid separating agent (the entrainer) forms one or more azeotropes with the other components in the mixture and causes two liquid phases to exist over a wide range of compositions, which is the key to making the distillation sequence work; (3) distillation using ionic salts, where the salts dissociate in the liquid mixture and alters the relative volatilities sufficiently that the separation become possible; (4) pressure-swing distillation where a series of column operating at different pressures are used to separate binary azeotropes that change appreciably in composition over a moderate pressure range or where a separating agent that forms a pressure-sensitive azeotrope is added to separate a pressure-insensitive azeotrope; and (5) reactive distillation where the separating agent reacts preferentially and reversibly with one of the azeotropic constitutes after which the reaction product is distilled from the nonreacting components and the reaction is reversed to recover the initial component.
In *simple distillation* a multicomponent liquid mixture is slowly boiled in a heated zone and the vapors are continuously removed as they form and, at any instant in time, the vapor is in equilibrium with the liquid remaining on the still. Because the vapor is always richer in the more volatile components than the liquid, the liquid composition changes continuously with time, becoming more and more concentrated in the least volatile species. A simple distillation residue curve is a means by which the changes in the composition of the liquid residue curves on the pot changes with time (Speight, 2014a). A residue curve map is a collection of the liquid residue curves originating from different initial compositions. Residue curve maps contain the same information as phase diagrams, but represent this information in a way that is more useful for understanding how to synthesize a distillation sequence to separate a mixture.

All of the residue curves originate at the light (lowest boiling) pure component in a region, move toward the intermediate boiling component, and end at the heavy (highest boiling) pure component in the same region. The lowest temperature nodes are termed as *unstable nodes*, as all trajectories leave from them; while the highest temperature points in the region are termed *stable nodes*, as all trajectories ultimately reach them. The point that the trajectories approach from one direction and end in a different direction (as always is the point of intermediate boiling component) is termed “saddle point.” Residue curve that divide the composition space into different distillation regions is called distillation boundaries.

Many different residue curve maps are possible when azeotropes are present. Ternary mixtures containing only one azeotrope may exhibit six possible residue curve maps that differ by the binary pair forming the azeotrope and by whether the azeotrope is minimum or maximum boiling. By identifying the limiting separation achievable by distillation, residue curve maps are also useful in synthesizing separation sequences combining distillation with other methods.

However, the separation of components of similar volatility may become economical 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 criterion that severely limits the application of extractive and azeotropic distillation. The majority of successful processes, in fact, 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 10°C–40°C (18°F–72°F) below that of the components. Thus, although the entrainer is more volatile than the components and distills off in the overhead product, it is present in a sufficiently high concentration in the rectification section of the column.

### 7.4.6 Extractive Distillation

*Extractive distillation* is the use of a third component to separate two close-boiling components in which one of the original components in the mixture is extracted by the third component and retained in the liquid phase to facilitate separation by distillation. In the process, the difference in volatility of the components to be separated is enhanced by the addition of a solvent or an entrainer.

Using acetone–water as an extractive solvent for butanes and butenes, butane is removed as overhead from the extractive distillation column with acetone–water charged at a point close to the top of the column. The bottom product of butenes and the extractive solvent are fed to a second column where the butenes are removed as overhead. The acetone–water solvent from the base of this column is recycled to the first column.

Extractive distillation (Figure 7.18) may also be used for the continuous recovery of individual aromatics, such as benzene, toluene, or xylene(s), from the appropriate petroleum fractions. *Prefractionation* concentrates a single aromatic cut into a close boiling cut, after which the aromatic concentrate is *extractively distilled* with a solvent (usually phenol) for benzene or toluene recovery. Mixed cresylic acids (cresol derivatives and methyl phenol derivatives) are used as the solvent for xylene recovery.
In general, none of the fractions or combinations of fractions separated from crude petroleum are suitable for immediate use as petroleum products. Each must be separately refined by treatments and processes that vary with the impurities in the fraction and the properties required in the finished product. The simplest treatment is the washing of a fraction with a lye solution to remove sulfur compounds. The most complex is the series of treatments—solvent treating, dewaxing, clay treating or hydrotreating, and blending—required to produce lubricating oils. On rare occasions no treatment of any kind is required. Some crude oils yield a light gas oil fraction that is suitable as furnace fuel oil or as a diesel fuel.

Extractive distillation is successful because the solvent is specially chosen to interact differently with the components of the original mixture, thereby altering their relative volatilities. Because these interactions occur predominantly in the liquid phase, the solvent is continuously added near the top of the extractive distillation column so that an appreciable amount is present in the liquid phase on all of the trays below. The mixture to be separated is added through second feed point further down the column. In the extractive column, the component having the greater volatility, not necessarily the component having the lowest boiling point, is taken overhead as a relatively pure distillate. The other component leaves with the solvent via the column bottoms. The solvent is separated from the remaining components in a second distillation column and then recycled back to the first column.

One of the most important steps in developing a successful (economical) extractive distillation sequence is selecting a good solvent. In general, selection criteria for the solvent include the following: the process (1) should enhance significantly the natural relative volatility of the key component, (2) should not require an excessive ratio of solvent to nonsolvent (because of cost of handling in the column and auxiliary equipment, (3) should not lead to the formation of two phases, and (4) should allow the desired product to be easily separable from the bottom product.

No single solvent or solvent mixture satisfies all of the criteria for use in extractive distillation. In general, none of the fractions or combinations of fractions separated from crude petroleum is suitable for immediate use as petroleum products. Each fraction must be separately refined by processes that vary with the impurities in the fraction and the properties required in the finished product (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). The simplest treatment is the washing of a fraction with a lye solution to remove sulfur compounds.
Two processes illustrate the similarities and differences between azeotropic distillation and extractive distillation. Both have been used for the separation of C₄ hydrocarbons (Figures 7.19 and 7.20). Thus, butadiene and butene may be separated by the use of liquid ammonia, which forms an azeotrope with butene. The ammonia–butene azeotrope overhead from the azeotropic distillation is condensed, cooled, and allowed to separate into a butene layer and a heavier ammonia layer. The butene layer is fed to a second column, where the ammonia is removed as a butene–ammonia azeotrope, and the remaining butene is recovered as bottom product. The ammonia layer is returned to the lower section of the first azeotropic distillation column. Butadiene is recovered as bottom product from this column.

FIGURE 7.19 Separation of butene and butadiene by azeotropic distillation.

FIGURE 7.20 Separation of butane and butene by extractive distillation.
7.5 OPTIONS FOR HEAVY FEEDSTOCKS

In order to further distill heavy oil, tar sand bitumen, or residuum, or topped crude, reduced pressure is required to prevent thermal cracking and the process takes place in one or more vacuum distillation towers. Since the heavy feedstocks are expected to contribute a growing fraction of hydrocarbon fuels production, changes can be expected in terms of the actual unit internals, unit operation, and prevention of corrosion. Innovations to the distillation units will most likely be more subtle than a complete restructuring of the distillation section of the refinery and will focus on (1) changes to the internal packing to prevent fouling within the distillation system, and (2) the use of metal alloy systems to mitigate corrosion.

7.5.1 DISTILLATION OPERATIONS

The principles of vacuum distillation resemble those of fractional distillation, and, except that larger-diameter columns are used to maintain comparable vapor velocities at the reduced pressures, the equipment is also similar. The internal designs of some vacuum towers are different from atmospheric towers in that random packing and demister pads are used instead of trays. A typical first-phase vacuum tower may produce gas oil, lubricating oil base stock, and a heavy residuum for propane deasphalting. A second-phase tower operating at lower vacuum may distill surplus residuum from the atmospheric tower, which is not used for lube-stock processing, and surplus residuum from the first vacuum tower not used for deasphalting.

Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum and heavy oil and tar sand bitumen have fewer components distilling at atmospheric pressure and under vacuum than conventional petroleum. Nevertheless, some heavy oil still pass through the distillation stage of a refinery before further processing is undertaken. In addition, a vacuum tower has recently been installed at the Syncrude Canada plant to offer an additional process option for upgrading tar sand bitumen (Speight, 2005, 2014a). The installation of such a tower as a means of refining heavy feedstocks (with the possible exception of the residua that are usually produced through a vacuum tower) is a question of economics and the ultimate goal of the refinery in terms of product slate. After distillation, the residuum from the heavy oil might pass to a cracking unit such as visbreaking or coking to produce salable products. Catalytic cracking of the residuum or the whole heavy oil is also an option but is very dependent on the constituents of the feedstock and their interaction with the catalyst.

Thus, there is the potential for applying a related concept to the deep distillation of the heavy feedstocks. The continued and projected increased influx of heavy oil, extra heavy oil, and tar sand bitumen into refineries will require reassessment of the need for refinery distillation. Nevertheless, vacuum distillation is an option for tar sand bitumen processes in which the distillation unit is employed to collect as much valuable high-vacuum gas oil as possible from the bitumen before the residuum is sent to a conversion unit. This option can assist in balancing the overall technical efficiency and economic efficiency of the bitumen refinery. Furthermore, if partial conversion (such as the use of visbreaking) is an option for processing heavy feedstocks or partial upgrading during recovery of the feedstock, distillation will still find a use in refineries.

Moreover, as feedstocks change in composition, the distillation unit will be required to achieve higher degrees of efficiency to produce the precursors to hydrocarbon fuels as well as feedstocks for other units that will eventually produce hydrocarbon fuels through cracking. This will more likely be achieved by changes in the internals of the distillation units as well as changes to the overlay use of the units. The overall effects will be for refineries to create the option to take deeper cuts into the crude oil feedstock leaving a harder resid to be used as feedstocks for the cracking units.

Catalytic distillation (reactive distillation) is a branch of reactive distillation that combines the processes of distillation and catalysis (Ng and Rempel, 2002; Harmsen, 2007). Catalytic distillation is a reactor technology that combines a heterogeneous catalytic reaction and the separation of...
reactants and products via distillation in a single reactor/distillation column. The heterogeneous catalyst provides the sites for catalytic reactions and also the interfacial surface for liquid/vapor separation. The distinct difference between the catalytic distillation column and the conventional distillation column lies in the placement of solid catalysts usually incorporated in a packing within the distillation column to provide a reaction section in addition to the traditional trays or random packings used for separations in the stripping the rectifying sections of the distillation column. Mass transfer characteristics of the catalytic distillation column packing in the reaction zone have significant influence on the product yield and selectivity. The benefits of catalytic distillation include energy and capital savings, enhanced conversion and product selectivity, longer catalyst lifetime, and reduction of waste streams. The first commercial application of CD was for the production of methyl tertiary butyl ether (MTBE). There are many other possible applications of CD such as the hydration of olefins, alkylation reactions, esterification reactions, hydrolysis, aldol condensation, hydrogenation, desulfurization, and oligomerization of olefins.

For example, catalytic distillation finds application for reversible reactions, such as methyl tetrabutyl ether (MTBE) and ethyl tributyl ether (ETBE) synthesis, so as to shift an unfavorable equilibrium by continuous reaction product withdrawal (DeCroocq, 1997). Catalytic distillation can provide also several advantages in selective hydrogenation of C₃, C₄, and C₅ cuts for petrochemical use. Inserting the catalyst in the fractionation column improves mercaptan derivatives removal, catalyst fouling resistance, and selective hydrogenation performances by modifying the reaction mixture composition along the column.

Fouling and foaming are frequent occurrence in distillation towers. Chemical reactions and surface phenomena in fouling and foaming systems can further complicate their predictability. Several techniques for dealing with such unpredictable problems include monitoring of tower conditions, selection of tower internals, and pretreatment of recycle streams. These methods will be improved and developed to the point where they are operative in all distillation units. Furthermore, distillation efficiency is limited by the undesired coke deposition, resulting in a significant loss of distillation efficiency. When a residuum is heated to pyrolysis temperatures (>350°C, 650°F), there is typically an induction period before coke formation begins. To avoid fouling, refiners often stop heating well before coke forms, using arbitrary criteria, but cessation of the heating can result in less than maximum distillate yield.

Over the past three decades, a better understanding of the chemistry and physics of coking has evolved (Chapter 5) (Speight, 2014a) and improved designs based on primary internals have allowed an increase in the amount of gas oil produced with increases in cut point from approximately 520°C (970°F) to 590°C (1095°F). As continuing inroads are made into the chemistry of coking, future distillation units will show improvements in the design of the internals leading to process equivalents of the laboratory spinning band distillation units. Thus, with the potential for an increase in the influx of heavy oil, tar sand bitumen, and biomass to refineries, there may be a resurgence of interest in the application of reactive distillation in refineries, which is a process where the still is also a chemical reactor. Separation of the product from the reaction mixture does not need a separate distillation step, which saves energy (for heating) and materials. This technique is especially useful for equilibrium-limited reactions and conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone. This helps reduce capital and investment costs and may be important for sustainable development due to a lower consumption of resources. The suitability of reactive distillation for a particular reaction depends on various factors such as volatility of the reactants and products along with the feasible reaction and distillation temperature. Hence, the use of reactive distillation for every reaction may not be feasible. Exploring the candidate reactions for reactive distillation is an area that needs considerable attention to expand the domain of reactive distillation processes.

However, the conditions in the reactive column are suboptimal both as a distillation column and a chemical reactor, since the reactive column combines these. In addition, the introduction of an in situ separation process in the reaction zone or vice versa leads to complex interactions between
Pretreatment and Distillation

vapor–liquid equilibrium, mass transfer rates, diffusion, and chemical kinetics, which poses a great challenge for design and synthesis of these systems. Side reactors, where a separate column feeds a reactor and vice versa, are better for some reactions if the optimal conditions of distillation and reaction differ too much.

**Membranes** may offer future alternatives to distillation. Membranes have started to enter the refinery for hydrogen recovery (see earlier) but are also being developed for other separations. Current membrane systems will probably be most effective in hybrid distillation processes to perform a first, crude, low-energy, low-cost separation, leaving the polishing operation for distillation. If high selectivity could be achieved with membranes, there is the potential to replace distillation in many separation processes.

### 7.5.2 Corrosion

Refinery distillation units run as efficiently as possible to reduce costs. One of the major issues that occurs in distillation units and decreases efficiency is corrosion of the metal components found throughout the process line of the hydrocarbon refining process (Speight, 2014b). Corrosion causes the failure of parts in addition to dictating the shutdown schedule of the unit, which can cause shutdown of the refinery. Attempts to block such corrosive influences will be a major issue of future refineries.

Furthermore, in addition to the corrosive properties of high-acid crude oils, sulfur may be present in crude oil as hydrogen sulfide (H$_2$S), as compounds (such as mercaptan derivatives, sulfide derivatives, disulfide derivatives, and thiophene derivatives), or as elemental sulfur. Each crude oil has different amounts and types of sulfur compounds but, generally, the proportion, stability, and complexity of the compounds are greater in heavier crude oils. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptan derivatives.

Heavy feedstocks (of the types that are relevant to this chapter, i.e., heavy oil, extra heavy oil, and tar sand bitumen) contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine). These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling. Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when crude is heated. Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH$_4$Cl), which causes fouling and corrosion.

The sections of the process susceptible to corrosion include (but may not be limited to) preheat exchanger (HCl and H$_2$S), preheat furnace and bottoms exchanger (H$_2$S and sulfur compounds), atmospheric tower and vacuum furnace (H$_2$S, sulfur compounds, and organic acids), vacuum tower (H$_2$S and organic acids), and overhead (H$_2$S, HCl, and water). Where sour crudes are processed, severe corrosion can occur in furnace tubing and in both atmospheric and vacuum towers where metal temperatures exceed 450°F. Wet hydrogen sulfide also will cause cracks in steel. When processing high-nitrogen crudes, nitrogen oxides can form in the flue gases of furnaces, and these oxides are corrosive to steel when cooled to low temperatures (nitric and nitrous acids are formed) in the presence of water.

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). However, the desalting operation does not always remove all of the corrosive elements and hydrogen chloride may be a product of the thermal treatment that occurs as part of the distillation process. 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.
Corrosion occurs in various forms in the distillation section of the refinery and is manifested by events such as pitting corrosion from water droplets, embrittlement from chemical attack if the dewatering and desalting unit has not operated efficiently, and stress corrosion cracking from sulfide attack.

High-temperature corrosion of distillation units will continue to be a major concern to the refining industry. The presence of naphthenic acid and sulfur compounds considerably increases corrosion in the high-temperature parts of the distillation units and equipment failures have become a critical safety and reliability issue. The difference in process conditions, materials of construction, and blend processed in each refinery and especially the frequent variation in crude diet increases the problem of correlating corrosion of a unit to a certain type of crude oil. In addition, a large number of interdependent parameters influence the high-temperature crude corrosion process.

Naphthenic acid corrosion is differentiated from sulfidic corrosion by the nature of the corrosion (pitting and impingement) and by its severe attack at high velocities in crude distillation units. Crude feedstock heaters, furnaces, transfer lines, feed and reflux sections of columns, atmospheric and vacuum columns, heat exchangers, and condensers are among the type of equipment subject to this type of corrosion.

From a materials standpoint, carbon steel can be used for refinery components. Carbon steel is resistant to the most common forms of corrosion, particularly from hydrocarbon impurities at temperatures below 205°C (400°F), but other corrosive chemicals and high-temperature environments prevent its use everywhere. Common replacement materials are low alloy steel containing chromium and molybdenum, with stainless steel containing more chromium dealing with more corrosive environments. More expensive materials commonly used are nickel titanium and copper alloys. These are primarily saved for the most problematic areas where extremely high temperatures or very corrosive chemicals are present.

Attempts to mitigate corrosion will continue to use a complex system of monitoring, preventative repairs, and careful use of materials. Monitoring methods include both offline checks taken during maintenance and online monitoring. Offline checks measure corrosion after it has occurred, telling the engineer when equipment must be replaced based on the historical information he has collected.

Blending of refinery feedstocks (with the inherent danger of phase separation and incompatibility) will continue to be used to mitigate the effects of corrosion as will blending, inhibition, materials upgrading, and process control. Blending will be used to reduce the naphthenic acid content of the feed, thereby reducing corrosion to an acceptable level. However, while blending of heavy and light crude oils can change shear stress parameters and might also help reduce corrosion, there is also the potential for incompatibility of heavy and light crude oils.

In summary, refinery distillation may appear to be waning in terms of under the processing of such heavy feedstocks but it is definitely not out.

REFERENCES
Pretreatment and Distillation


