8 Thermal Cracking Processes

8.1 INTRODUCTION

Distillation (Chapter 7) has remained a major refinery process, and almost every crude oil that enters a refinery is subjected to this process. However, not all crude oils yield the same distillation products. In fact, the nature of the crude oil dictates the processes that may be required for refining. And balancing product yield with demand is a necessary part of refinery operations (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). However, the balancing of product yield and market demand, without the manufacture of large quantities of fractions having low commercial value, has long required processes for the conversion of hydrocarbons of one molecular weight range and/or structure into some other molecular weight range and/or structure. Basic processes for this are still the so-called cracking processes in which relatively high-boiling constituents carbons are cracked, that is, thermally decomposed into lower-molecular-weight, smaller, lower-boiling molecules, although reforming alkylation, polymerization, and hydrogen-refining processes have wide applications in making premium-quality products (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

After 1910 and the conclusion of World War I, the demand for automotive (and other) fuels began to outstrip the market requirements for kerosene and refiners, needing to stay abreast of the market pull, were pressed to develop new technologies to increase gasoline yields. There being finite amounts of straight-run distillate fuels in crude oil, refiners had, of necessity, the urgency to develop processes to produce additional amounts of these fuels. The conversion of coal and oil shale to liquid through the agency of cracking had been known for centuries, and the production of various spirits from petroleum though thermal methods had been known since at least the inception of Greek fire in earlier centuries.

The discovery that higher-molecular-weight (higher-boiling) materials could be decomposed to lower-molecular-weight (lower-boiling) products was used to increase the production of kerosene and was called cracking distillation. In the process, a batch of crude oil was heated until most of the kerosene was distilled from it and the overhead material became dark in color. At this point the still fires were lowered, the rate of distillation decreased, and the heavy oils were held in the hot zone, during which time some of the large hydrocarbons were decomposed and rearranged into lower-molecular-weight products. After a suitable time, the still fires were increased and distillation continued in the normal way. The overhead product, however, was light oil suitable for kerosene instead of the heavy oil that would otherwise have been produced. Thus, it was not surprising that such technologies were adapted for the fledgling petroleum industry.

The earliest processes, which involved thermal cracking, consisted of heating heavier oils (for which there was a low market requirement) in pressurized reactors and thereby cracking, or splitting, their large molecules into the smaller ones that form the lighter, more valuable fractions such as gasoline, kerosene, and light industrial fuels. Gasoline manufactured by thermal cracking processes performed better in automobile engines than gasoline derived from straight distillation of crude petroleum. The development of more powerful aircraft engines in the late 1930s gave rise to a need to increase the combustion characteristics of gasoline to improve engine performance. Thus, during World War II and the late 1940s, improved refining processes involving the use of catalysts led to further improvements in the quality of transportation fuels and further increased their supply. These improved processes, including catalytic cracking of residua and other heavy feedstocks (Chapter 9), alkylation (Chapter 13), polymerization (Chapter 13), and isomerization (Chapter 13),
enabled the petroleum industry to meet the demands of high-performance combat aircraft and, after the war, to supply increasing quantities of transportation fuels.

The 1950s and 1960s brought a large-scale demand for jet fuel and high-quality lubricating oils. The continuing increase in demand for petroleum products also heightened the need to process a wider variety of crude oils into high-quality products. Catalytic reforming of naphtha (Chapter 13) replaced the earlier thermal reforming process and became the leading process for upgrading fuel qualities to meet the needs of higher-compression engines. Hydrocracking, a catalytic cracking process conducted in the presence of hydrogen (Chapter 11), was developed to be a versatile manufacturing process for increasing the yields of either gasoline or jet fuels.

In the early stages of thermal cracking process development, processes were generally classified as either liquid phase, high pressure (350–1500 psi), low temperature (400°C–510°C, 750°F–950°F) or vapor phase, low pressure (less than 200 psi), high temperature (540°C–650°C, 1000°F–1200°F). In reality, the processes were mixed phase with no process really being entirely liquid or vapor phase, but the classification (like many classifications of crude oil and related areas) was still used as a matter of convenience (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

The early were classified as liquid-phase processes and had the following advantages over vapor-phase processes: (1) large yields of gasoline of moderate octane number, (2) low gas yields, (3) ability to use a wide variety of charge stocks, (4) long cycle time due to low coke formation, and (5) flexibility and ease of control. However, the vapor-phase processes had the advantages of operation at lower pressures and the production of a higher-octane gasoline due to the increased production of olefins and light aromatics. However, there were many disadvantages that curtailed the development of vapor-phase processes: (1) temperatures were required which the steel alloys available at the time could not tolerate, (2) there were high gas yields and resulting losses since the gases were normally not recovered, and (3) there was a high production of olefinic compounds that created naphtha with poor stability (increased tendency to form undesirable gum) (Mushrush and Speight, 1995; Speight, 2014) that required subsequent treating of the gasoline to stabilize it against gum formation. The vapor-phase processes were not considered suitable for the production of large quantities of gasoline but did find application in petrochemical manufacture due to the high concentration of olefins produced.

It is generally recognized that the most important part of any refinery, after the distillation units, is the gasoline (and liquid fuels) manufacturing facilities; other facilities are added to manufacture additional products as indicated by technical feasibility and economic gain. More equipment is used in the manufacture of gasoline, the equipment is more elaborate, and the processes more complex than for any other product. Among the processes that have been used for liquid fuels production are thermal cracking, catalytic cracking, thermal reforming, catalytic reforming, polymerization, alkylation, coking, and distillation of fractions directly from crude petroleum (Figure 8.1). Each of these processes may be carried out in a number of ways, which differ in details of operation, or essential equipment, or both (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

Thermal processes are essentially processes that decompose, rearrange, or combine hydrocarbon molecules by the application of heat. The major variables involved are feedstock type, time, temperature, and pressure and, as such, are usually considered in promoting cracking (thermal decomposition) of the heavier molecules to lighter products and in minimizing coke formation. Thus, one of the earliest processes used in the petroleum industry is the noncatalytic conversion of higher-boiling petroleum stocks into lower-boiling products, known as thermal cracking.

The thermal decomposition (cracking) of high-molecular-weight hydrocarbons to lower-molecular-weight and normally more valuable hydrocarbons has long been practiced in the petroleum refining industry. Although catalytic cracking has generally replaced thermal cracking, noncatalytic cracking processes using high temperature to achieve the decomposition are still in operation. In several cases, thermal cracking processes to produce specific desired products or
Thermal Cracking Processes

Conventional thermal cracking is the thermal decomposition, under pressure, of high-molecular-weight constituents (higher molecular weight and higher boiling than gasoline constituents) to form lower-molecular-weight (and lower-boiling) species. Thus, the thermal cracking process is

to dispose of specific undesirable charge streams are being operated or installed. The purpose of this chapter is to provide basic information to assist the practicing engineer/petroleum refiner to (1) determine if a particular thermal cracking process would be suitable for a specific application and could fit into the overall operation, (2) develop a basic design for a thermal cracking process, and (3) operate an existing or proposed process.

Conventional thermal cracking is the thermal decomposition, under pressure, of high-molecular-weight constituents (higher molecular weight and higher boiling than gasoline constituents) to form lower-molecular-weight (and lower-boiling) species. Thus, the thermal cracking process is

FIGURE 8.1 Schematic representation of a refinery showing placement of the various conversion units.
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designed to produce gasoline from higher-boiling charge stocks, and any unconverted or mildly cracked charge components (compounds which have been partially decomposed but are still higher boiling than gasoline) are usually recycled to extinction to maximize gasoline production. A moderate quantity of light hydrocarbon gases is also formed. As thermal cracking proceeds, reactive unsaturated molecules are formed that continue to react and can ultimately create higher-molecular-weight species that are relatively hydrogen deficient and readily form coke. Thus, they cannot be recycled without excessive coke formation and are therefore removed from the system as cycle fuel oil.

When petroleum fractions are heated to temperatures over 350°C (660°F), the rates of the thermal cause thermal decomposition to proceed at significant rates (Speight, 2000, 2014). Thermal decomposition does not require the addition of catalyst; therefore, this approach is the oldest technology available for residue conversion. The severity of thermal processing determines the conversion and the product characteristics. Thermal treatment of residues ranges from mild treatment for reduction of viscosity to ultrapyrolysis (high-temperature cracking at very short residence time) for complete conversion to olefins and light ends. The higher the temperature, the shorter the time required to achieve a given conversion but, in many cases, with a change in the chemistry of the reaction. The severity of the process conditions is the combination of reaction time and temperature to achieve a given conversion.

Thermal reactions, however, can give rise to a variety of different reactions so that selectivity for a given product changes with temperature and pressure. The mild- and high-severity processes are frequently used for processing of residua, while conditions similar to ultrapyrolysis (high temperature and very short residence time) are only used commercially for cracking ethane, propane, butane, and light distillate feeds to produce ethylene and higher olefins. Sufficiently high temperatures convert oils entirely to gases and coke; cracking conditions are controlled to produce as much as possible of the desired product, which is usually gasoline but may be cracked gases for petrochemicals or a lower viscosity oil for use as a fuel oil. The feedstock, or cracking stock, may be almost any fraction obtained from crude petroleum, but the greatest amount of cracking is carried out on gas oils, a term that refers to the portion of crude petroleum boiling between the fuel oils (kerosene and/or stove oil) and the residuum. Residua are also cracked, but the processes are somewhat different from those used for gas oils.

Thus, thermal conversion processes are designed to increase the yield of lower-boiling products obtainable from petroleum either directly (by means of the production of gasoline components from higher-boiling feedstocks) or indirectly (by production of olefins and the like, which are precursors of the gasoline components). These processes may also be characterized by the physical state (liquid and/or vapor phase) in which the decomposition occurs. The state depends on the nature of the feedstock as well as conditions of pressure and temperature.

From the chemical viewpoint the products of cracking are very different from those obtained directly from crude petroleum—the products are nonindigenous to petroleum because they are created from petroleum by application of an external force (heat). When a 12-carbon atom hydrocarbon typical of straight-run gas oil is cracked or broken into two parts, one may be a 6-carbon paraffin hydrocarbon and the other a 6-carbon olefin hydrocarbon:

\[
\text{CH}_3\text{(CH}_2\text{)}_6\text{CH}_3 \rightarrow \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_3 + \text{CH}_2=\text{CH(CH}_2\text{)}_3\text{CH}_3
\]

The paraffin may be the same as is found in straight-run (distilled) gasoline, but the olefin is new. Furthermore, the paraffin has an octane number approaching 0 but the olefin has an octane number approaching 100. Hence naphtha formed by cracking (cracked gasoline) has a higher octane number than straight-run gasoline. In addition to a large variety of olefins, cracking produces high-octane aromatic and branched-chain hydrocarbons in higher proportions than are found in straight-run gasoline. Diolefins are produced but in relatively small amounts; they are undesirable in gasoline because they readily combine to form gum. The overall complexity of such a reaction is illustrated
by the following equations in which the products are subject to the position of bond scission within
the starting molecule:

\[
\begin{align*}
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_8CH_3 + CH_2=CH_2 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_7CH_3 + CH_2=CHCH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_6CH_3 + CH_2=CHCH_2CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_5CH_3 + CH_2=CH(CH_2)_2CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_4CH_3 + CH_2=CH(CH_2)_3CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_3CH_3 + CH_2=CH(CH_2)_4CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3(CH_2)_2CH_3 + CH_2=CH(CH_2)_5CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3CH_2CH_3 + CH_2=CH(CH_2)_6CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_3CH_3 + CH_2=CH(CH_2)_7CH_3 \\
CH_3(CH_2)_{10}CH_3 & \rightarrow CH_4 + CH_2=CH(CH_2)_8CH_3
\end{align*}
\]

Furthermore, the primary products (unless the reaction conditions are monitored carefully) will
react further to yield secondary, tertiary, and even quaternary products.

The hydrocarbons with the least thermal stability are the paraffins, and the olefins produced by
the cracking of paraffins are also reactive. Cycloparaffin derivatives (napthene derivatives) are less
easily cracked, their stability depending mainly on any side chains present, but ring splitting may
occur, and dehydrogenation can lead to the formation of unsaturated napthenes and aromatics.
Aromatics are the most stable (refractory) hydrocarbons, the stability depending on the length and
stability of side chains. Very severe thermal cracking of high-molecular-weight constituents can
result in the production of excessive amounts of coke.

The higher-boiling oils produced by cracking are light and heavy gas oils as well as a residual oil,
which in the case of thermal cracking is usually (erroneously) called tar and in the case of catalytic
cracking is called cracked fractionator bottoms. The residual oil may be used as heavy fuel oil, and
gas oils from catalytic cracking are suitable as domestic and industrial fuel oils or as diesel fuels if
blended with straight-run gas oils. Gas oils from thermal cracking must be mixed with straight-run
(distilled) gas oils before they become suitable for domestic fuel oils and diesel fuels.

The gas oils produced by cracking are an important source of gasoline and, in a once-through
cracking operation, all of the cracked material is separated into products and may be used as such.
However, the cracked gas oils are more resistant to cracking (more refractory) than straight-run gas
oils but can still be cracked to produce more gasoline. This is done in a recycling operation in which
the cracked gas oil is combined with fresh feed for another trip through the cracking unit. The opera-
tion may be repeated until the cracked gas oil is almost completely decomposed (cracking to extinc-
tion) by recycling (recycling to extinction) the higher-boiling product, but it is more usual to withdraw
part of the cracked gas oil from the system according to the need for fuel oils. The extent to which
recycling is carried out affects the amount or yield of cracked gasoline resulting from the process.

The gases formed by cracking are particularly important because of their chemical properties
and their quantity. Only relatively small amounts of paraffinic gases are obtained from crude oil,
and these are chemically inactive. Cracking produces both paraffinic gases (e.g., propane, C_3H_8) and
olefinic gases (e.g., propene, C_3H_6); the latter are used in the refinery as the feed for polymerization
plants where high-octane polymer gasoline is made. In some refineries, the gases are used to make alkylate, a high-octane component for aviation gasoline and for motor gasoline. In particular, the cracked gases are the starting points for many petrochemicals (Speight, 2014).

The importance of solvents in coking has been recognized for many years (Langer et al., 1961, 1962), but their effects have often been ascribed to hydrogen-donor reactions rather than phase behavior. The separation of the phases depends on the solvent characteristics of the liquid. Addition of aromatic solvents will suppress phase separation while paraffins will enhance separation. Microscopic examination of coke particles often shows evidence for the presence of a mesophase, which are spherical domains that exhibit the anisotropic optical characteristics of liquid crystal. This phenomenon is consistent with the formation of a second liquid phase; the mesophase liquid is denser than the rest of the hydrocarbon, has a higher surface tension, and likely wets metal surfaces better than the rest of the liquid phase. The mesophase characteristic of coke diminishes as the liquid phase becomes more compatible with the aromatic material (Speight, 1990, 2000).

Thermal cracking of higher-boiling materials to produce motor gasoline is now becoming an obso-lete process, since the antiknock requirement of modern automobile engines has outstripped the ability of the thermal cracking process to supply an economical source of high-quality fuel. New units are rarely installed, but a few refineries still operate thermal cracking units built in previous years.

In summary, the cracking of petroleum constituents can be visualized as a series of simple thermal conversions (Chapter 5). The reactions involve the formation of transient highly reactive spe-cies that may react further in several ways to produce the observed product slate (Germain, 1969; Speight, 2000, 2014). Thus, even though chemistry and physics can be used to explain feedstock reactivity the main objective of feedstock evaluation (Chapter 2) is to allow a degree of predictability of feedstock behavior in thermal processes (Speight, 2000, 2014). And in such instances, chemical principles must be combined with engineering principles to understand feedstock processability and predictability of feedstock behavior. In the simplest sense, process planning can be built on an understanding of the following three parameter groups (Speight, 2015a): (1) feedstock properties, (2) process parameters, and (3) equipment parameters.

**Feedstock properties** such as carbon residue (potential coke formation), sulfur content (hydrogen needs for desulfurization), metallic constituents (catalyst rejuvenation), nitrogen content (catalyst rejuvenation), naphthenic or paraffinic character through the use of a characterization factor or similar indicator (potential for cracking in different ways to give different products), and, to a lesser extent, asphaltene content (coke formation) since this last parameter is related to several of the previous parameters.

**Process parameters** such as time–temperature–pressure relationships (distillate and coke yields), feedstock recycle ratio (distillate and coke yields plus overall conversion), and coke formation (lack of liquid production when liquids are the preferred products).

**Equipment parameters** such as batch operation, semicontinuous operation, or continuous operation (residence time and contact with the catalyst, if any), coke removal, and unit capacity that also dictates residence time.

However, it is not the purpose of this text to present the details of these three categories but they should be kept in mind when considering and deciding upon the potential utility of any process presented throughout this and subsequent chapters.

### 8.2 THERMAL CRACKING

As the demand for gasoline increased with the onset of automobile sales, the issue of how to pro-duce more gasoline from less crude oil was solved in 1913 by the incorporation of cracking units into refinery operations in which fractions higher boiling than gasoline were converted into gasoline by thermal decomposition.
The origins of cracking are unknown. There are records that illustrate the use of naphtha in Greek fire almost 2000 years ago (Speight, 2014), but whether the naphtha was produced naturally by distillation or by cracking distillation is not clear. Cracking was used commercially in the production of oils from coal and oil shale before the beginning of the modern petroleum industry. From this, the discovery that the higher-boiling materials from petroleum could be decomposed to lower-molecular-weight products was used to increase the production of kerosene and was called cracking distillation (Kobe and McKetta, 1958).

The precise origins of the modern version of cracking distillation, as applied in the modern petroleum industry, are also unknown. However, it is essential to recognize that the production of volatile product by the destructive distillation of wood and coal was known for many years, if not decades or centuries, before the birth of the modern petroleum industry. Indeed, the production of spirits of fire (i.e., naphtha, the flammable constituent of Greek fire) was known from early times. The occurrence of bitumen at Hit (Mesopotamia) that was used as mastic by the Assyrians was further developed for use in warfare though the production of naphtha by destructive distillation.

At the beginning of the twentieth century, the yields of gasoline and kerosene fractions were usually markedly increased by means of cracking distillation, but the technique was not entirely suitable for gasoline production. As the need for gasoline arose, the necessity of prolonging the cracking process became apparent and led to a process known as pressure cracking which is a batch operation in which feedstock was heated to approximately 425°C (800°F) in stills (shell stills) especially reinforced to operate at pressures as high as 95 psi for 24 hours. Distillation was then started and, during the next 48–72 hours, a low-boiling distillate was obtained, which was treated with sulfuric acid to remove unstable gum-forming components (olefins and diolefins) and then redistilled to produce a naphtha (cracked gasoline, boiling range <205°C, <400°F) and residual fuel oil (Stephens and Spencer, 1956).

The Burton cracking process for the large-scale production of naphtha (cracked gasoline) was first used in 1912. The process employed batch distillation in horizontal shell stills and operated at approximately 400°C (ca. 750°F) and 75–95 psi and was the first successful method of converting higher-boiling feedstocks to gasoline. However, batch heating gas oil was considered inefficient, and during the years 1914–1922 a number of successful continuous cracking processes were developed. In these processes gas oil was continuously pumped through a unit that heated the gas oil to the required temperature, held it for a time under pressure, and then the cracked product was discharged into a distillation unit for separation into gases, gasoline, gas oil, and cracked residuum (often called tar).

The tube and tank cracking process is typical of the early continuous cracking processes. Gas oil, preheated by exchange with the hot products of cracking, was pumped into the cracking coil (up to several hundred feet long) that lined the inner walls of a furnace where oil or gas burners raised the temperature of the gas oil to 425°C (800°F). The hot gas oil passed from the cracking coil into a reaction chamber (soaker) where the gas oil was held under these temperature and pressure conditions until the cracking reactions to be completed. The cracking reactions formed coke, which over the course of several days filled the soaker. The gas oil stream was then switched to a second soaker, and drilling operations similar to those used in drilling an oil well cleaned out the first soaker. The cracked material (other than coke) left the onstream soaker to enter an evaporator (tar separator) maintained under a much lower pressure than the soaker, where, because of the lower pressure, all the cracked material except the tar became vaporized. The vapor left the top of the separator, where it was distilled into separate fractions: gases, gasoline, and gas oil. The tar that was deposited in the separator was pumped out for use as asphalt or as a heavy fuel oil.

Shortly thereafter, in 1921, a more advanced thermal cracking process which operated at 750°F–860°F (400°C–460°C) was developed (Dubbs process). In the process, a reduced crude (such as an atmospheric residuum or a topped crude oil) was the feedstock and the process also employed the concept of recycling in which the gas oil was combined with fresh (heavy) feedstock for further cracking. In a typical application of conventional thermal cracking (Figure 8.2),
the feedstock (reduced crude, i.e., residuum or flashed crude oil) is preheated by direct exchange with the cracked products in the fractionating columns. Cracked gasoline and middle distillate fractions were removed from the upper section of the column. Light and heavy distillate fractions were removed from the lower section and are pumped to separate heaters. Higher temperatures were used to crack the more refractory light distillate fraction. The streams from the heaters were combined and sent to a soaking chamber, where additional time is provided to complete the cracking reactions. The cracked products were then separated in a low-pressure flash chamber where a heavy fuel oil is removed as bottoms. The remaining cracked products were sent to the fractionating columns.

As refining technology evolved throughout the twentieth century, the feedstocks for cracking processes became the residuum or gas oil from a distillation unit. In addition, the residual oil produced as the end product of distillation processes, and even some of the higher-boiling crude oil constituents, often contains substantial amounts of asphaltic materials, which preclude use of the residuum as fuel oils or lubricating stocks (Speight, 2000, 2014; Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007).

However, subjecting these residua directly to thermal processes has become economically advantageous since, on the one hand, the end result is the production of lower-boiling products but, on the other hand, the asphaltene constituents and the resin constituents that are concentrated in residua are precursors to high yields of thermal coke (i.e., coke formed in noncatalytic processes) (Chapter 3). Although new thermal cracking units are now under development for heavy oil and tar sand bitumen (Speight, 2008, 2014), processes that can be regarded as having evolved from the original concept of thermal cracking are visbreaking and the various coking processes (Speight, 2014).

Low pressures (<100 psi) and temperatures in excess of 500°C (930°F) tend to produce lower-molecular-weight hydrocarbons than those produced at higher pressures (400–1000 psi) and at temperatures below 500°C (930°F). The reaction time is also important; light feeds (gas oils) and recycle oils require longer reaction times than the readily cracked heavy residues. Recycle of the light oil (middle distillate or fuel oil) fraction also affects the product slate of the thermal cracker.
(Table 8.1). Mild cracking conditions (defined here as a low conversion per cycle) favor a high yield of gasoline components with low gas and coke production, but the gasoline quality is not high, whereas more severe conditions give increased gas and coke production and reduced gasoline yield (but of higher quality). With limited conversion per cycle, the heavier residues must be recycled. However, the recycled oils become increasingly refractory upon repeated cracking, and if they are not required as a fuel oil stock they may be subjected to a coking operation to increase gasoline yield or refined by means of a hydrogen process.

8.3 VISBREAKING

Visbreaking (viscosity reduction, viscosity breaking), a mild form of thermal cracking, was developed in the late 1930s to produce more desirable and valuable products (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Stell et al., 2009a,b; Carrillo and Corredor, 2013; Speight, 2014). The processes regarded as having evolved from the original concept of thermal cracking are visbreaking and the various coking processes (Table 8.2). The process is a relatively mild, liquid-phase thermal cracking process used to convert heavy, high viscosity feedstocks to lower viscosity fractions suitable for use in heavy fuel oil. This ultimately results in less production of fuel oil since less cutter stock (low viscosity diluent) is required for blending to meet fuel oil viscosity specifications. The cutter stock no longer required in fuel oil may then be used in more valuable products. A secondary benefit from the visbreaking operation is the production of gas oil and gasoline streams that usually have higher product values than the visbreaker charge. Visbreaking produces a small quantity of light hydrocarbon gases and a larger amount of gasoline and remains a process of promise for heavy feedstocks (Stark and Falkler, 2008; Stark et al., 2008).

### Table 8.1

**Example of Thermal Cracking in Reduced Crude (Flasher Residuum)**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>API gravity</th>
<th>IBP 227.0°C; 440.0°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracking parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>500.0°; 930.0°F</td>
<td></td>
</tr>
<tr>
<td>Soaker pressure</td>
<td>225.0 psig; 1550.0 kPa</td>
<td></td>
</tr>
<tr>
<td>Product yields, vol%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasolinea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphtha</td>
<td>57.5</td>
<td></td>
</tr>
<tr>
<td>Heating oil (light oil)</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Residuum</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>API gravity</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>Heating oilb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Naphtha</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>Heating oil (light oil)</td>
<td>23.0</td>
<td></td>
</tr>
<tr>
<td>Residuum</td>
<td>34.0</td>
<td></td>
</tr>
<tr>
<td>API gravity</td>
<td>8.0</td>
<td></td>
</tr>
</tbody>
</table>

*a* Light oil recycle.

*b* No recycle of light oil.

Visbreaking (viscosity reduction, viscosity breaking), a mild form of thermal cracking, was developed in the late 1930s to produce more desirable and valuable products (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Stell et al., 2009a,b; Carrillo and Corredor, 2013; Speight, 2014). The processes regarded as having evolved from the original concept of thermal cracking are visbreaking and the various coking processes (Table 8.2). The process is a relatively mild, liquid-phase thermal cracking process used to convert heavy, high viscosity feedstocks to lower viscosity fractions suitable for use in heavy fuel oil. This ultimately results in less production of fuel oil since less cutter stock (low viscosity diluent) is required for blending to meet fuel oil viscosity specifications. The cutter stock no longer required in fuel oil may then be used in more valuable products. A secondary benefit from the visbreaking operation is the production of gas oil and gasoline streams that usually have higher product values than the visbreaker charge. Visbreaking produces a small quantity of light hydrocarbon gases and a larger amount of gasoline and remains a process of promise for heavy feedstocks (Stark and Falkler, 2008; Stark et al., 2008).
The process can also be used as the first step in upgrading heavy feedstocks (Schucker, 2003). In such a process, the heavy feedstock is first thermally cracked using visbreaking or hydrovisbreaking technology to produce a product that is lower in molecular weight and boiling point than the feed. The product is then deasphalted using an alkane solvent at a solvent-to-feed ratio of less than 2 wherein separation of solvent and deasphalted oil from the asphaltenes is achieved through the use of a two-stage membrane separation system in which the second stage is a centrifugal membrane.

Visbreaking, unlike conventional thermal cracking, typically does not employ a recycle stream. Conditions are too mild to crack a gas oil recycle stream and the unconverted residual stream, if recycled, would cause excessive heater coking. The boiling range of the product residual stream is extended by visbreaking so that light and heavy gas oils can be fractionated from the product residual stream, if desired. In some present applications, the heavy gas oil stream is recycled and cracked to extinction in a separate higher-temperature heater with the production of products that are lower boiling than the original feedstock (Table 8.3) (Ballard et al., 1992; Speight and Ozum, 2002; Parkash, 2003; Negin and Van Tine, 2004; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). Low residence times are required to avoid polymerization and coking reactions, although additives can help to suppress coke deposits on the tubes of the furnace.
### TABLE 8.3
Examples of Product Yields and Product Properties for Visbreaking Various Feedstocks

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Feedstock</th>
<th>Feedstock</th>
<th>Feedstock</th>
<th>Feedstock</th>
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<td></td>
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<td></td>
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<tr>
<td>Gravity, API</td>
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<tr>
<td>Carbon residuea</td>
<td>10.6</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>Naphtha (&lt;425°F; &lt;220°C)</td>
<td>6.2</td>
<td>8.0</td>
<td>7.8</td>
<td>7.8</td>
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<td>8.1</td>
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<td></td>
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<td>Carbon residuea</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>0.6</td>
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<td>3.2</td>
<td>5.0</td>
<td>4.7</td>
<td>4.6</td>
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* Conradson.

b A blank product yield line indicates that the yield of the lower-boiling product has been included in the yield of the higher-boiling product.
Visbreaking conditions range from 455°C to 510°C (850°F to 950°F) at a short residence time and from 50 to 300 psi at the heating coil outlet. It is the short residence time that brings to visbreaking the concept of being a mild thermal reaction in contrast to, for example, the delayed coking process where residence times are much longer and the thermal reactions are allowed to proceed to completion. The visbreaking process uses a quench operation to terminate the thermal reactions. Liquid-phase cracking takes place under these low-severity conditions to produce some naphtha, as well as material in the kerosene and gas oil boiling range. The gas oil may be used as additional feed for catalytic cracking units, or as heating oil.

There are two visbreaking processes, which are available commercially (Figure 8.3), the first process is the coil, or furnace, type and the second is the soaker type: (1) the coal visbreaking process and (2) the soaker visbreaking process. In the coil visbreaking unit (sometimes referred to as the furnace visbreaking unit), the cracking process occurs in the furnace tubes (or coils). Material exiting the furnace is quenched to halt the cracking reactions: frequently this is achieved by heat exchange with the virgin material being fed to the furnace, which in turn is a good energy efficiency step—a stream of cold oil (such as gas oil) is used to the same effect after which the gas oil is recovered and reused. The extent of the cracking reaction is controlled by regulation of the speed of flow of the oil through the furnace tubes. The quenched oil then passes to a fractionator where the products of the cracking (gas, LPG, gasoline, gas oil, and tar) are separated and recovered.

The coil visbreaking process (Figure 8.4) achieves conversion by high-temperature cracking within a dedicated soaking coil in the furnace. With conversion primarily achieved as a result of temperature and residence time, coil visbreaking is described as a high-temperature, short-residence-time route. The main advantage of the coil-type design is the two-zone fired heater that provides better control of the material being heated and, with the coil-type design, decoking of the heater tubes is accomplished more easily by the use of steam–air decoking.

In the alternative soaker visbreaking process (Figure 8.5), the bulk of the cracking reaction occurs not in the furnace but in a drum located after the furnace (the soaker) in which the heated feedstock is held at an elevated temperature for a predetermined period of time to allow cracking to occur before being quenched and then passed to a fractionator. In soaker visbreaking, lower temperatures are used than in coil visbreaking. Consequently, the soaker visbreaking process is described as a low-temperature, high-residence-time route. Product quality and yields from the coil and soaker drum design are essentially the same at a specified severity being independent of visbreaker configuration. By providing the residence time required to achieve the desired reaction,
the soaker drum design allows the heater to operate at a lower outlet temperature (thereby saving fuel) but there are disadvantages.

In the process, the heavy feedstock is passed through a furnace where it is heated to a temperature of 480°C (895°F) under an outlet pressure of approximately 100 psi. The cracked products are then passed into a flash-distillation chamber. The overhead material from this chamber is then fractionated to produce naphtha and light gas oil. The liquid products from the flash chamber are cooled with a gas oil flux and then sent to a vacuum fractionator. This yields a heavy gas oil distillate and a residuum of reduced viscosity—a 5%–10% v/v conversion of residuum to naphtha is usually sufficient to afford at least an approximate fivefold reduction in viscosity. Reduction in viscosity is also accompanied by a reduction in the pour point. An alternative option is to use lower furnace temperatures and longer times, achieved by installing a soaking drum between the furnace and the fractionator. The disadvantage of this approach is the need to remove coke from the soaking drum.

The higher heater outlet temperature specified for a coil visbreaker is an important advantage of coil visbreaking. The higher heater outlet temperature is used to recover significantly higher quantities of heavy visbroken gas oil. This capability cannot be achieved with a soaker visbreaker...
without the addition of a vacuum flasher. In terms of product yield, there is little difference between the two options (soaker visbreaker compared to coil visbreaker) approaches. However, each offers significant advantages in particular situations. For example, the cracking reaction forms coke as a by-product. In coil visbreaking, this lays down in the tubes of the furnace and will eventually lead to fouling or blocking of the tubes. The lower temperatures used in the soaker approach mean that these units use less fuel. In cases where a refinery buys fuel to support process operations, any savings in fuel consumption could be extremely valuable. In such cases, soaker visbreaking may be advantageous. In fact, most of the existing visbreaker are the soaker type, which utilize a soaker drum in conjunction with a fired heater to achieve conversion and which reduces the temperature required to achieve conversion while producing a stable residue product, thereby increasing the heater run length and reducing the frequency of unit shutdown for heater decoking.

Decoking is accomplished by a high-pressure water jet. First, the top and bottom heads of the coke drum are removed after which a hole is drilled in the coke from the top to the bottom of the vessel and a rotating stem is lowered through the hole, spraying a water jet sideways. The high-pressure jet cuts the coke into lumps, which fall out the bottom of the drum for subsequent loading into trucks or railcars for shipment to customers. Typically, coke drums operate on fixed cycles that depend upon the feedstock and the coking parameters. Cokers produce no liquid residue but yield up to 30% coke by weight. Much of the low-sulfur product is employed to produce electrodes for the electrolytic smelting of aluminum.

The main disadvantage is the decoking operation of the heater and soaker drum and, although decoking requirements of the soaker drum design are not as frequent as those of the coil-type design, the soaker design requires more equipment for coke removal and handling. The customary practice of removing coke from a drum is to cut it out with high-pressure water thereby producing a significant amount of coke-laden water that needs to be handled, filtered, and then recycled for use again.

The Shell soaker visbreaking process is suitable for the production of fuel oil by residuum (atmospheric residuum, vacuum residuum, or solvent deasphalter bottoms) and viscosity reduction with a maximum production of distillates. The basic configuration of the process includes the heater, soaker, and fractionator and more recently a vacuum flasher to recover more distillate products (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). The cut point of the HGO stream taken from the vacuum flasher is approximately 520°C (970°F). In the process, the feedstock is preheated before entering the visbreaker heater, where the residue is heated to the required cracking temperature. Heater effluent is sent to the soaker drum where most of the thermal cracking and viscosity reduction takes place under controlled conditions. Soaker drum effluent is flashed and then quenched in the fractionator and the flashed vapors are fractionated into gas, naphtha, gas oil, and visbreaker residue. The visbreaker residue is steam stripped in the bottom of the fractionator and pumped through the cooling circuit for further processing. Visbreaker gas oil, which is recovered as a side stream, is steam stripped, cooled, and sent for further processing. As expected, product yields are dependent on feed type and product specifications. The heavy gas oil stream for the visbreaker can be used as feedstock for a thermal distillate cracking unit or for a catalytic cracker for the production of lower-boiling distillate products.

Other variations of visbreaking technology include the Tervahl-T and Tervahl-H processes. The Tervahl-T alternative (Figure 8.6) includes only the thermal section to produce a synthetic crude oil with better transportability by having reduced viscosity and greater stability. The Tervahl-H alternative adds hydrogen that also increases the extent of the desulfurization and decreases the carbon residua. The Aquaconversion process (Figure 8.7) is a hydrovisbreaking process that uses catalyst-activated transfer of hydrogen from water added to the feedstock. Reactions that lead to coke formation are suppressed and there is no separation of asphaltene-type material (Marzin et al., 1998).

Visbreaking conditions range from 455°C to 510°C (850°F to 950°F) at a short residence time and from 50 to 300 psi at the heating coil outlet. It is the short residence time that brings to visbreaking the concept of being a mild thermal reaction. This is in contrast to, for example, the delayed coking process where residence times are much longer and the thermal reactions are allowed to
Thermal Cracking Processes

Thermal reactions proceed to completion. The visbreaking process uses a quench operation to terminate the thermal reactions. Liquid-phase cracking takes place under these low-severity conditions to produce some naphtha, as well as material in the kerosene and gas oil boiling range. The gas oil may be used as additional feed for catalytic cracking units or as heating oil.

Atmospheric and vacuum residua are the usual feedstocks to a visbreaker although extra heavy oil and tar sand bitumen are also likely feedstocks. The heavy feedstocks will typically achieve a conversion to gas, naphtha, and gas oil in the order of 10%–50% w/w, depending on the severity and feedstock characteristics. The conversion of the residua to distillate (low-boiling products) is commonly used as a measurement of the severity of the visbreaking operation and the conversion is determined as the amount of 345°C+ (650°F+) material present in the atmospheric residuum or the 482°C+ (900°F+) material present in the vacuum residuum that is converted (visbroken) into lower-boiling components.

The extent of feedstock conversion is limited by a number of feedstock characteristics, such as asphaltene content (Figure 8.8) that varies with the type of feedstock and, hence the type of residuum, and, more particularly, carbon residue (Figure 8.9). In very general terms, paraffinic feedstocks will have a low heptane–asphaltene content (0%–8% by weight) whereas naphthenic feedstock will have a much higher heptane–asphaltene content (10%–20% by weight) with the mixed crude oils having intermediate values. Of course, when the heptane–asphaltenes are
concentrated in the residua (through distillation), the proportions of the asphaltenes will be much higher. Thus, feedstocks with a high heptane–asphaltene content will result in an overall lower conversion than feedstocks with a lower heptane–asphaltene content while maintaining production of a stable fuel oil from the visbreaker bottoms. Minimizing the sodium content to almost a negligible amount and minimizing the Conradson carbon weight percent will result in longer cycle run lengths.

In addition, variations in feedstock quality will impact the level of conversion obtained at a specific severity. For example, for a given feedstock, as the severity is increased, the viscosity of the 205°C (400°F) visbroken residue (often referred to as *visbroken tar* or *visbreaker tar*) initially decreases and then, at higher severity levels, increases dramatically, indicating the formation of coke precursors and their initial phase separation as sediment. The point at which this viscosity reversal occurs differs from feedstock to feedstock but can be estimated from the amount of low-molecular-weight hydrocarbon gases (≤C₃) (Negin and Van Tine, 2004).

![Figure 8.8](image1.png) **Figure 8.8** Relationship of visbreaker conversion to asphaltene content.

![Figure 8.9](image2.png) **Figure 8.9** Relationship of visbreaker conversion time to feedstock carbon residue.
Thus, a crude oil residuum is passed through a furnace where it is heated to a temperature of 480°C (895°F) under an outlet pressure of approximately 100 psi. The heating coils in the furnace are arranged to provide a soaking section of low heat density, where the charge remains until the visbreaking reactions are completed. The cracked products are then passed into a flash-distillation chamber. It is advisable to maintain the flash zone temperature as low as possible to minimize the potential for coking. Under fixed flashing conditions, increasing the yield of the residuum will reduce this temperature.

The overhead material from this chamber is then fractionated to produce a low-quality gasoline as an overhead product and light gas oil as bottoms. The liquid products from the flash chamber are cooled with a gas oil flux and then sent to a vacuum fractionator. This yields a heavy gas oil distillate and a residuum of reduced viscosity. A quench oil may also be used to terminate the reactions and will also influence the temperature of the flash zone.

A 5%–10% v/v conversion of atmospheric residua to naphtha is usually sufficient to afford at least an approximate fivefold reduction in viscosity. Reduction in viscosity is also accompanied by a reduction in the pour point. However, the reduction in viscosity of distillation residua tends to reach a limiting value with conversion, although the total product viscosity can continue to decrease. The minimum viscosity of the unconverted residue can lie outside the range of allowable conversion if sediment begins to form. When shipment of the visbreaker product by pipeline is the process objective, addition of a diluent such as gas condensate can be used to achieve a further reduction in viscosity.

Conversion of residua in visbreaking follows first-order reaction kinetics. The minimum viscosity of the unconverted residue can lie outside the range of allowable conversion if sediment begins to form. When pipelining of the visbreaker product is the process objective, addition of a diluent such as gas condensate can be used to achieve a further reduction in viscosity.

Briefly, fouling (a deposit buildup in refinery processes that impedes heat transfer and/or reduces throughput) is the leading cause of diminished efficiency and productivity in refineries. The energy lost due to this inefficiency must be supplied by burning additional fuel or reducing feed. While most fouling is caused by the deposition of heavier hydrocarbon species coming directly from the crude oil, a small undetermined percentage is related to corrosion and scale deposits, either actively participating as loose corrosion products or by scale acting as a substrate for hydrocarbon deposition. Fouling will also occur in the drum of a soaker visbreaker, though the lower temperatures used in the soaker drum lead to fouling at a much slower rate. Coil visbreaking units therefore require frequent decoking. Soaker drums require far less frequent attention but their being taken out of service normally requires a complete halt to the operation.

Thus, the severity of the visbreaking operation is generally limited by the stability of the visbroken product—generally a prelude to the onset of fouling. If over-cracking occurs, the resulting fuel oil may form excessive deposits in storage or when used as a fuel in a furnace. The visbreaking correlations presented are based on operating to levels where the fuel oil quality will be limited by this test. This severity level is well within the operating limits that would be imposed by excessive coke formation in properly designed visbreaking furnaces.

The main limitation of the visbreaking process, and for that matter all thermal processes is that the products can be unstable. Thermal cracking at low pressure gives olefins, particularly in the naphtha fraction. These olefins give a very unstable product, which tends to undergo secondary reactions to form gum and intractable residua. Product stability of the visbreaker residue is a main concern in selecting the severity of the visbreaker operating conditions. Severity, or the degree of conversion, can cause phase separation of the fuel oil even after cutter stock blending. Increasing visbreaking severity and percent conversion will initially lead to a reduction in the visbroken fuel oil viscosity. However, visbroken fuel oil stability will decrease as the level of severity—and hence conversion—is increased beyond a certain point, dependent on feedstock characteristics.

The instability of the visbroken fuel oil is related to the asphaltene constituents and their thermal present in the residuum. Asphaltenes are heavy nonvolatile compounds that can be classified...
according to their solubility in various solvents. The asphaltene constituents can be thermally altered during visbreaking operations. In addition, during visbreaking, some of the high-molecular-weight constituents, including some of the asphaltene constituents, are converted to lower-boiling and medium-boiling paraffinic components, some of which are removed from the residuum. The asphaltenes and thermally altered, being unchanged, are thus concentrated in the product residuum (that may contain new paraffinic material) and if the extent of the visbreaking reaction is too high, the asphaltene constituents or altered asphaltene constituents will phase tend to precipitate in the product fuel oil, creating an unstable fuel oil.

A common method of measuring the amount of asphaltenes in petroleum is by addition of a low-boiling liquid hydrocarbon such as \( n \)-pentane (ASTM D 893, ASTM D2007) or \( n \)-heptane (ASTM D3279, ASTM D4124) by which treatment the asphaltenes separate as a solid (Speight, 2000, 2014). Since the amount of asphaltenes in the visbreaking unit charge residuum may limit the severity of the visbreaking operations, the \( n \)-pentane insoluble content or \( n \)-heptane insoluble content of the feedstock is used as the correlating parameter in various visbreaking correlations. However, these correlations can be visbreaker and feedstock dependent and application from one unit to another and one feedstock to another may be misleading.

Sulfur in the visbroken residuum can also be an issue since the sulfur content of the visbreaker residuum is often higher (approximately 0.5% w/w or greater) than the sulfur in the feedstock. Therefore, it can be difficult to meet the commercial sulfur specifications of the refinery product residual fuel oil, and blending with low-sulfur cutter stocks may be required.

Visbreaking, like thermal cracking, is a first-order reaction. However, due to the visbreaking severity limits imposed by fuel oil instability, operating conditions do not approach the level where secondary reactions, polymerization and condensation, occur to any significant extent. The first-order reaction rate equation altered to fit the visbreaking reaction is

\[
K = \left( \frac{1}{t} \right) \left( \frac{\ln 100}{X_1} \right)
\]

where
- \( K \) is the first-order reaction velocity constant, \( 1/s \)
- \( t \) is the time at thermal conversion conditions, \( s \)
- \( X_1 = 900°F \) visbroken residuum yield, vol\%

A simplified graphical representation of the yields of the various product with conversion can be constructed (Figure 8.10) with the understanding that different feedstocks will require different graphical presentations.

The visbreaking reaction is first order and velocity constant data as a function of visbreaking furnace outlet temperature can be presented graphically (Figure 8.11). The thermal conversion reactions are generally assumed to start at 425°C (800°F) although some visbreaking occurs below this temperature. Therefore, the residence time in the 425°C–450°C (800°F–865°F) reaction zone should be 613 seconds.

The central piece of equipment in any thermal process is, and visbreaking is with no exception, the heater. The heater must be adequate to efficiently supply the heat required to accomplish the desired degree of thermal conversion. A continually increasing temperature gradient designed to give most of the temperature increase in the front part of the heater tubes with only a slow rate of increase near the outlet is preferred. Precision control of time and temperature is usually not critical in the processes covered in this article. Usually, all that is required is to design to some target temperature range and then adjust actual operations to achieve the desired cracking. In the higher-temperature processes (e.g., ethylene manufacture), temperature control does become of prime importance due to equilibrium considerations.
Equipment design to minimize coke formation is of importance. The excessive production of coke adversely affects the thermal cracking process in the following ways: (1) reduces heat transfer rates, (2) increases pressure drops, (3) creates overheating, (4) reduces run time, and (5) requires the expense of removing the coke from the equipment. In addition, the metallurgy of the equipment, specifically the heater tubes and pumps, in the high temperature, corrosive environments must be
adequate to prevent expensive destruction and replacement of equipment. In the early days of thermal cracking, the metallurgy of the heater tubes was not of sufficient quality to permit extended periods of high temperatures. Modern improvements in the quality of steel have extended the durability of the thermal cracking equipment.

The advances in heater design have reached a point where very efficient furnace and heating tube arrangements can be built that give the refiner the desired thermal cracking operation. The practice of the refiner is generally to set the specifications the heater is expected to meet for the specific application and have a heater manufacturer prepare a suitable design. Proper tube size selection depends upon minimizing pressure drop while obtaining good turbulence for proper heat transfer that is also dependent upon the charge rate (Table 8.4) that ultimately affects the residence time and, therefore, the extent of the conversion.

The charge stock liquid velocity should be sufficient to provide enough turbulence to ensure a good rate of heat transfer and to minimize coking. A minimum linear cold 15.6°C (60°F) velocity on the order of 5 ft/s for a 100% liquid charge rate is considered to be sufficient. The maximum velocity would be limited to approximately 10 ft/s due to excessive pressure drop. The velocities at the higher cracking temperatures would, of course, be greater due to the partial vaporization of the charge.

Most of the heat supplied to the charge stock is radiant heat. The convection section of the heater is used primarily to supply preheat to the charge prior to the main heating in the radiant section. The heat transfer rate in the convection section will range from 3,000 to 10,000 Btu/ft²/h. The heating rates in the radiant section will range from 8,000 to 20,000 Btu/ft²/h depending upon the charge stock, with heavier oil generally requiring the lower heating rate.

The heating tube outlet temperature will depend upon the charge stock being processed and the degree of thermal conversion required. The outlet temperature will vary from a minimum of 425°C (800°F) for visbreaking to a maximum of 595°C (1100°F) for thermal reforming. The combustion chamber temperature will range from 650°C to 870°C (1200°F to 1600°F) at a point approximately 1 ft below the radiant tubes. Flue gas temperatures are usually high (425°C–595°C, 800°F–1100°F) particularly since the heavy charge stock is usually entering the heater at a high temperature from a fractionating tower. An exception to the charge entering at a high temperature would be when charging gasoline to a thermal reformer. However, since thermal reforming requires high temperatures, flue gas temperatures will also be high.

Since it is desirable to maintain different temperature increase rates throughout the charge heating, that is, rapid increase at the beginning of the heating coil and a lower rate near the outlet, zone temperature control within the furnace is desired. A three-zone furnace is preferred with the first zone giving the greatest rate of temperature increase and the last zone the least.

### Table 8.4

<table>
<thead>
<tr>
<th>Total Charge Rate (Fresh Feed + Recycle) (bbl/Day)</th>
<th>Internal Diameter of Tube (inch)</th>
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<tbody>
<tr>
<td>3,000</td>
<td>2 – 3</td>
</tr>
<tr>
<td>6,000</td>
<td>3 – 4</td>
</tr>
<tr>
<td>12,000</td>
<td>4 – 41/2</td>
</tr>
</tbody>
</table>

*a Parallel tubes of smaller diameters would be preferable to one large tube. In this case, two 3 inch diameter parallel tubes may be preferred.*
Coke formation limits the operation of the heater, and techniques should be employed to minimize coke formation in the heater tubes. Coking occurs on the walls of the tubes, particularly where turbulence is low and temperature is high. Maintaining sufficient turbulence assists in limiting coke formation. Baffles within the tubes are sometimes used but water injection into the charge stream is the preferred method. Water is usually injected at the inlet although water also may be injected at additional points along the heater tubes. The water, in addition to providing turbulence in the heater tubes as it is vaporized to steam, also provides a means to control temperature. The optimum initial point of water injection into the heater tubes is at the point of incipient cracking where coke would start to form. An advantage to this injection point is the elimination of the additional pressure drop that would have been created by the presence of water between the heater inlet and the point of incipient cracking.

The preferred method to remove coke (decoke) from the heater tubes is to burn off the coke using a steam–air mixture. The heater tubes, therefore, should be capable of withstanding temperatures up to 760°C (1400°F) at low pressures for limited time periods. The heater tubes along with the tube supports should be designed to handle the thermal expansion extremes that would be encountered. Mechanical means, such as drills, can also be used to remove coke, but most modern heaters use the steam–air combustion technique. Parallel heaters may be employed so that one can be decoked while permitting cracking to proceed in the other heater(s).

The metallurgy of thermal cracking units is variable although alloy steel tubes of 7%–9% chromium are usually satisfactory to resist sulfur corrosion in thermal cracking heaters. If the hydrogen sulfide content of the cracked products exceeds 0.1 mol% in the cracking zone, a higher alloy steel may be required. Stabilized stainless steel, such as Type 321 or 347, would be suitable in this case. Other alloys, such as the Inconel or Incoloy alloys, could also be used. Seamless tubes with welded return bends are now normally used in heaters. Flanged return bends were used in earlier thermal cracking units to facilitate cleaning. However, use of steam air to burn out the coke essentially eliminates the need for flanged fittings that, in turn, reduces the possibility of dangerous leaks.

A useful tool to aid in the design and operation of thermal cracking units is the soaking volume factor (SVF). This factor combines time, temperature, and pressure of thermal cracking operations into a single numerical value. The SVF is defined as the equivalent coil volume in cubic feet per daily barrel of charge (fresh plus recycle) if the cracking reaction had occurred at 800°F and 750 psi:

\[
\text{SVF}_{750\text{psi}/800\text{F}} = \frac{1}{F}RK_p dV
\]

where

- \( \text{SVF}_{750\text{psi}/800\text{F}} \) is the SVF at base reaction conditions of 750 psi gauge pressure and 800°F, cubic feet of coil volume per total charge throughput in barrels per day
- \( F \) is the charge (fresh plus recycle) throughput rate, barrels per day
- \( R \) is the ratio of reaction velocity constant at temperature \( T \) and reaction velocity constant at 800°F
- \( K_p \) is the pressure correction factor for pressures other than 750 psi gauge
- \( dV \) is the incremental coil volume, cubic feet

The ratio of reaction velocity constants may be obtained from graphical formats (Figure 8.12) and should not be obtained from such plots of reaction velocity constants since there is a correction for the effect of temperature on the volume of the reacting material that needs to be corrected and incorporated into ion; this correction has been incorporated into the data (Figure 8.13). The pressure correction factor, \( K_p \), may be obtained graphically (Figure 8.14).
When an additional soaking drum is used, the SYF for the soaking drum should be added to the coil SVF. The SVF for the drum may be determined from:

\[
SVF_D = \frac{DV}{F(K_{TD})(K_p)}
\]

where
- \(SVF_D\) is the SVF of the drum
- \(DV\) is the volume of drum, ft\(^3\)
- \(F\) is the charge (fresh plus recycle) throughput rate, bbl/day
- \(K_{TD}\) is the reaction velocity constant for the mean drum temperature
- \(K_p\) is the pressure correction factor for the mean drum pressure

The SVF will range from 0.03 for visbreaking of heavy residual stocks to approximately 1.2 for light gas oil cracking. The SVF is a numerical expression of cracking rate and thus can be correlated with product yield and quality. SVF may also be translated into cracking coils and still volumes of known dimensions under design conditions of temperature and pressure.

A cracking unit seldom operates very long at design conditions. Charge stock quality changes, desired product yields and qualities change, or additional capacity is required. These changes require a SVF that is different than the design SVF. The SVF may be varied by (1) varying pressure at constant temperature and feed rate; (2) varying temperature at constant feed rate, the pressure gradient varying with the effect upon cracking rate and fluid density in the cracking coil; and
(3) varying the soaking volume at constant temperature and pressure by varying heater feed rate and/or varying the number of tubes in the section above 425°C (800°F).

With the advent of higher firing rate, better efficiency heaters, the use of external soaking drums to provide additional reaction times is of less importance in thermal cracking operations. In modern units the coil in the heater is usually sufficient to provide the temperature–time relationships required. A possible exception would be the case where it is desirable to crack a considerable amount of heavy residual stock. The temperature required probably could not be successfully obtained in a heater coil without excessive coking. A reaction chamber (soaking drum) is employed where the hotter, cleaner light gas oil is used to supply heat to the heavier dirty oil stream in a soaking drum. A low-temperature light gas oil stream is also frequently used to wet the walls of the soaking drum to minimize coking. Parallel soakers could be used to allow one to be decoked while the other is used for the cracking operations.

The pumps used in thermal cracking operations must be capable of operation for extended periods handling a high temperature (above 230°C, 450°F, and up to 345°C, 650°F) corrosive liquid. In addition, since coke particles are formed in thermal cracking, the pumps must be able to withstand the potential erosion of the metal parts by the coke particles. In the early days of thermal

![First-order reaction velocity constants for thermal cracking.](image)

\[
K = \frac{1}{t} \ln \frac{100}{100-x}
\]

where,

- \( K \) = Reaction velocity constant, 1/s
- \( t \) = Time, second
- \( x \) = Gasoline yield, vol%

**FIGURE 8.13** First-order reaction velocity constants for thermal cracking.
cracking, reciprocating pumps were commonly used. In later units, centrifugal pumps have been used. A preferred centrifugal pump would be of the coke-crushing type or may have open impellors with case wear plates substituted for the front rings. The metal should be 12% chromium steel alloy or a higher alloy if serious corrosion is potential.

Heat exchangers should be constructed to provide easy cleaning since the high temperatures and coke particles can create extensive fouling of the exchangers. The downstream processing equipment (flash drums, separators, fractionating towers) are typically of standard design, and no special design specifications are required other than minimizing potential coke buildup. This can be accomplished by designing the equipment so there would be no significant holdup or dormant spots in the process equipment where coke could accumulate.

In thermal cracking operations there is a considerable amount of excess heat that cannot be economically utilized within the cracking unit itself. When a thermal cracking unit is being considered, it is desirable to construct the unit in conjunction with some other unit, such as a crude still, which could utilize the excess heat to preheat the crude oil charge. Alternately, the excess heat could be used in steam generation facilities.

Visbreaking may be the most underestimated and/or undervalued process in a refinery. The process may find rejuvenated use not only for heavy feedstock (including tar sand bitumen) but also for biofeedstocks. These visbreaking processes posses sufficient hardware flexibility to accommodate feedstock blending (petroleum feedstocks and biofeedstocks) and of the unit as well as a high measure of reliability and predictive operations/maintenance, thereby minimizing unplanned shutdowns.

The severity of visbreaker operation is generally limited by the stability requirement of the product as well as the extent of fouling and coke laydown in the visbreaker heater (Speight, 2015a). The former requirement means that the stability of the residue must be sufficient to ensure that the finished fuel resulting from blending with diluents (that are less aromatic than the residue) is stable.

---

FIGURE 8.14  Pressure correction for the SVF with pressure in excess of 750 psig (5170 kPa).
Thermal Cracking Processes

and that asphaltene flocculation does not occur. Where the residue is converted to an emulsion, blend stability is improved and severity/conversion can be increased, subject to acceptable levels of heater fouling and coke deposition (Miles, 2009). Operational modifications, such as increasing steam injection or recycling heavy distillates from the visbreaker fractionator, may help mitigate coking tendency and enhance yield, while some relatively low-cost options to increase heater capacity might be implemented in certain instances.

In terms of processing biofeedstocks, many biofeedstocks have a high oxygen content and high mineral content which could (even when blended) disqualify the use of the biomaterial as a feedstock to a hydroprocessing unit. Refiners are very wary of high-oxygen and high-mineral feedstocks because of the increased hydrogen requirements (hydrogen is an expensive refinery commodity) to remove the oxygen from the hydrocarbon products with the appearance of the additional hydrogen as water. However, blending a biofeedstock with a resid as feedstock to a visbreaking unit to produce additional fuel products is a concept that could pay dividends and provide refineries with a source of fuels to supplement petroleum feedstocks. In the visbreaker, the feedstock is converted to overhead (volatile products) and coke (if the unit is operated beyond the typical operating point or coke-forming threshold) (Speight, 2014). The majority of the nitrogen, sulfur, and minerals appear in the coke. Oxygen often appears in the volatile product as water and carbon dioxide, unfortunately removing valuable hydrogen from the internal hydrogen management system.

Alternatively, another option is the preparation of a feedstock that is acceptable to a refinery. In particular, any process that reduces the mineral matter in the biofeedstock and reduces the oxygen content in the biofeed would be a benefit.

This can be accomplished by one or two preliminary treatment steps (such as the visbreaking process) in which the feedstock is demineralized and the oxygen constituents are removed as overhead (volatile) material giving the potential for the production of a fraction rich in oxygen functions that may be of some use to the chemical industry. Such a process might have to be established at a biofeedstock production site, unless the refinery has the means by which to accommodate the feedstock in an already existing unit.

In a manner similar to the visbreaking process where the biofeedstock is blended with a residuum, the biofeedstock alone would be heated in a visbreaker-type reactor (at a lower temperature than the conventional visbreaking temperature) to the point where hydrocarbons (or alcohols) are evolved and coke starts to form. As the coke forms, the mineral matter is deposited with the coke and the oxygen constituents are deoxygenized leaving a (predominantly) hydrocarbon product, which as a liquid that will ensure easy separation from the coke and mineral matter.

8.4 COKING

Coking is a thermal process for the continuous conversion of residua into lower-boiling products. The feedstock can be atmospheric residuum, vacuum residuum, or cracked residuum and the products are gases, naphtha, fuel oil, gas oil, and coke. Coking processes generally utilize longer reaction times than thermal cracking processes. To accomplish this, drums or chambers (reaction vessels) are employed, but it is necessary to use two or more such vessels so that coke removal can be accomplished in those vessels not onstream without interrupting the semicontinuous nature of the process. Gas oil may be the major product of a coking operation and serves primarily as a feedstock for catalytic cracking units. The coke can be used as fuel but processing for specialty uses, such as electrode manufacture, production of chemicals, and metallurgical coke, is also possible. For these latter uses, the coke may require treatment to remove sulfur and metal impurities—calcined petroleum coke can be used for making anodes for aluminum manufacture and a variety of carbon or graphite products such as brushes for electrical equipment.

Thus, coking is a thermal cracking-type operation used to convert low-grade feedstocks such as straight-run and cracked residua to coke, gas, and distillates. Two types of petroleum coking processes are presently operating: (1) delayed coking, which uses multiple coking chambers to permit continuous
feed processing wherein one drum is making coke and one drum is being decoked; and (2) fluid coking, which is a fully continuous process where product coke can be withdrawn as a fluidized solid.

Crude oil residua obtained from the vacuum distillation tower as a nonvolatile (bottoms) fraction, heavy oil, and tar sand bitumen are the usual feedstocks to coking units. Atmospheric tower bottoms (long residua) may be charged to coking units but it is generally not attractive to thermally degrade the gas oil fraction contained in the longer residua. Other feedstocks to coking units are deasphalter bottoms (often referred to as deasphalter pitch) and tar sand bitumen, and cracked residua (thermal tars). The products are gases, naphtha, fuel oil, gas oil, and coke. The gas oil may be the major product of a coking operation and serves primarily as a feedstock for catalytic cracking units. The coke obtained is usually used as fuel, but processing for specialty uses, such as electrode manufacture, production of chemicals, and metallurgical coke, is also possible and increases the value of the coke. For these uses, the coke may require treatment to remove sulfur and metal impurities. Furthermore, the increasing attention paid to reducing atmospheric pollution has also served to direct some attention to coking, since the process not only concentrates such pollutants as feedstock sulfur in the coke but also usually yields products that can be conveniently subjected to desulfurization processes.

Coking processes have the virtue of eliminating the residue fraction of the feed, at the cost of forming a solid carbonaceous product. The yield of coke in a given coking process tends to be proportional to the carbon residue content of the feed (measured as the Conradson carbon residue) (Speight, 2014, 2015b). The data (Table 8.5) illustrate how the yield of coke from delayed and fluid coking varies with Conradson carbon residue of the feed. The formation of large quantities of coke is a severe drawback unless the coke can be put to use. Calcined petroleum coke can be used for making anodes for aluminum manufacture and a variety of carbon or graphite products such as brushes for electrical equipment. These applications, however, require a coke that is low in mineral matter and sulfur.

If the feedstock produces a high-sulfur, high-ash, high-vanadium coke, one option for use of the coke is combustion of the coke to produce process steam (and large quantities of sulfur dioxide unless the coke is first gasified or the combustion gases are scrubbed). Another option is stockpiling. For some feedstocks, particularly from heavy oil, the combination of poor coke properties for anode use, limits on sulfur dioxide emissions, and loss of liquid product volume have tended to relegate coking processes to a strictly secondary role in any new upgrading facilities.

### 8.4.1 Delayed Coking

_Delayed coking_ is the oldest, most widely used process and has changed very little since the process was first brought onstream approximately 80 years ago. It is a semicontinuous (semibatch) process in which the heated charge is transferred to large coking (or soaking) drums that provide the long

<table>
<thead>
<tr>
<th>Carbon Residue (wt%)</th>
<th>°API</th>
<th>Coke Yield, Delayed Coker</th>
<th>Weight % Fluid Coker</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>8.5</td>
<td>11.5</td>
</tr>
<tr>
<td>10</td>
<td>16</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>27.5</td>
<td>23</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>35.5</td>
<td>29</td>
</tr>
<tr>
<td>25</td>
<td>3.5</td>
<td>42</td>
<td>34.5</td>
</tr>
<tr>
<td>40</td>
<td>−2.5</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>
residence time needed to allow the cracking reactions to proceed to completion (McKinney, 1992; Feintuch and Negin, 2004). The process (Figure 8.15) is widely used for treating residua and is particularly attractive when the green coke produced can be sold for anode or graphitic carbon manufacture or when there is no market for fuel oils. The process uses long reaction times in the liquid phase to convert the residue fraction of the feed to gases, distillates, and coke. The condensation reactions that give rise to the highly aromatic coke product also tend to retain sulfur, nitrogen, and metals, so that the coke is enriched in these elements relative to the feed.

In the process (Figure 8.15), the feedstock is charged to the fractionator and subsequently charged with an amount of recycle material (usually approximately 10%, but as much as 25%, of the total feedstock) from the coker fractionator through a preheater and then to one of a pair of coke drums; the heater outlet temperature varies from 480°C to 515°C (895°F to 960°F) to produce the various products (Table 8.6). The cracked products leave the drum as overheads to the fractionator and coke deposits form on the inner surface of the drum. The majority of the sulfur originally in the feedstock remains in the coke (Table 8.7). A pair of coke drums is used so that while one drum is on stream, the other is being cleaned allowing continuous processing and the drum operation cycle is typically 48 hours (Table 8.8). The temperature in the coke drum ranges from 415°C to 450°C (780°F to 840°F) at pressures from 15 to 90 psi (103 to 620 kPa).

Fractionators separate the overhead products from the coke drum into fuel gas (low-molecular-weight gases up to and including ethane), propane and propylene (CH₃CH₂CH₃–CH₃CH=CH₂), butane–butene (CH₃CH₂CH₂CH₃–CH₃CH₂CH=CH₂), naphtha, light gas oil, and heavy gas oil. Yields and product quality vary widely due to the broad range of feedstock used for coking units (Table 8.6).

Coker naphtha typically has a boiling range of up to 220°C (430°F), is olefinic, and must be upgraded by hydrogen processing for removal of olefins and sulfur. They are then used conventionally for reforming to gasoline or as chemical feedstocks. Middle distillates, boiling in the range of 220°C–360°C (430°F–680°F), are also hydrogen treated for improved storage stability, sulfur removal, and nitrogen reduction. They can then be used for either diesel or burner fuels or thermally processed to lower-boiling naphtha. The gas oil boiling up to approximately 510°C (950°F) end
<table>
<thead>
<tr>
<th>Feedstock</th>
<th>API gravity</th>
<th>Carbon residue(^c)</th>
<th>Sulfur, wt%</th>
<th>Naphtha</th>
<th>Light gas oil(^a)</th>
<th>Heavy gas oil</th>
<th>Coke</th>
<th>Sulfur, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Louisiana Residuum</td>
<td>12.3</td>
<td>6.7</td>
<td>0.7</td>
<td>22.8</td>
<td>18.4</td>
<td>37.6</td>
<td>23.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Kuwait Residuum</td>
<td>13.0</td>
<td>19.8</td>
<td>5.2</td>
<td>26.7</td>
<td>28.0</td>
<td>18.4</td>
<td>30.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Kuwait Residuum(^b)</td>
<td>16.1</td>
<td>9.1</td>
<td>0.7</td>
<td>22.0</td>
<td>41.9</td>
<td>19.1</td>
<td>18.5</td>
<td>1.7</td>
</tr>
<tr>
<td>West Texas Residuum</td>
<td>8.9</td>
<td>17.8</td>
<td>3.0</td>
<td>28.9</td>
<td>16.5</td>
<td>26.4</td>
<td>28.4</td>
<td>4.5</td>
</tr>
<tr>
<td>West Texas Residuum(^b)</td>
<td>15.2</td>
<td>9.3</td>
<td>0.6</td>
<td>20.1</td>
<td>31.7</td>
<td>27.5</td>
<td>20.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Oklahoma Residuum</td>
<td>13.0</td>
<td>14.1</td>
<td>1.2</td>
<td>10.7</td>
<td>20.4</td>
<td>16.7</td>
<td>23.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Oklahoma Residuum(^b)</td>
<td>16.8</td>
<td>8.0</td>
<td>1.6</td>
<td>22.5</td>
<td>20.4</td>
<td>16.7</td>
<td>20.8</td>
<td>1.6</td>
</tr>
<tr>
<td>California Residuum</td>
<td>12.0</td>
<td>9.4</td>
<td>1.6</td>
<td>15.7</td>
<td>36.5</td>
<td>72.3</td>
<td>19.1</td>
<td>1.6</td>
</tr>
<tr>
<td>California Residuum(^b)</td>
<td>12.3</td>
<td>9.6</td>
<td>0.4</td>
<td>16.0</td>
<td>36.5</td>
<td>56.5</td>
<td>21.6</td>
<td>3.0</td>
</tr>
<tr>
<td>Midcontinent Residuum</td>
<td>7.4</td>
<td>9.4</td>
<td>0.4</td>
<td>12.6</td>
<td>36.5</td>
<td>50.8</td>
<td>21.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Middle East Residuum</td>
<td>8.2</td>
<td>9.6</td>
<td>0.4</td>
<td>17.4</td>
<td>50.8</td>
<td>48.5</td>
<td>24.9</td>
<td>5.3</td>
</tr>
<tr>
<td>Middle East Residuum(^b)</td>
<td>2.6</td>
<td>23.3</td>
<td>4.4</td>
<td>10.0</td>
<td>50.3</td>
<td>50.3</td>
<td>31.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Venezuela Residuum</td>
<td>35 psig compared to ~14–18 psig for the oilier delayed cokers.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) A blank product line indicates that the yield of the lower-boiling product has been included in the yield of the higher-boiling product.

\(^b\) Hydrodesulfurized.

\(^c\) Conradson.

\(^d\) 35 psig compared to ~14–18 psig for the oilier delayed cokers.
point may be charged to a fluid catalytic cracking unit immediately or after hydrogen upgrading when low sulfur is a requirement.

As noted earlier (Table 8.8), the coke drums are on a 48-hour cycle. The coke drum is usually onstream for approximately 24 hours before becoming filled with porous coke after which time the coke is removed by the following procedure: (1) the coke deposit is cooled with water; (2) one of the heads of the coking drum is removed to permit the drilling of a hole through the center of the deposit; and (3) a hydraulic cutting device, which uses multiple high-pressure water jets, is inserted into the hole and the wet coke is removed from the drum. Typically, 24 hours is required to complete the cleaning operation and to prepare the coke drum for subsequent use onstream (Table 8.8).

A well-designed delayed coker will have an operating efficiency of better than 95%, although delayed coking units are generally scheduled for shutdown for cleaning and repairs on a 12- to 18-month schedule, depending on the most economical cycle for the refinery. In terms of process efficiency, the feedstock heater and the coke drums are the most critical parts of the delayed coking process. The function of the heater or furnace is to preheat the charge quickly, to avoid preliminary decomposition, to the required temperature. Since coking is endothermic, the furnace outlet temperature must be approximately 55°C (100°F) higher than the coke drum temperature to provide the necessary process heat. The heater run length is a function of coke laydown in heater tubes, and careful design is necessary to avoid premature shutdown with cycle lengths preferably at least 1 year. When the charge stock is derived from crude distillation, double desalting is desirable since salt deposits will shorten heater cycles.

The heater for a delayed coking unit does not require as broad and operating range as a thermal cracking or visbreaking heater where both contact time and temperature can be varied to achieve
the desired level of conversion. The coker heater must reach a fixed outlet temperature for the
required coke drum temperatures. Thus, the coker heater requires a short residence time, high radi-
ant heat flux, and good control of heat distribution.

The function of the coke drum is to provide the residence time required for the coking reactions
to proceed to completion and to accumulate the coke. In sizing coke drums, a superficial vapor
velocity in the range of 0.3–0.5 ft/s is used and coke drums with heights of 97 ft (30 m) have been
constructed and approach a practical limit for hydraulic coke cutting. Drum diameters up to 26 ft
(8 m) have been commonly used, and larger drums are feasible for efficient processing. Various
types of level detectors are used to permit drum filling to within 7–8 ft (2–2.5 m) of the upper
tangent line of the drum monitor coke height in the drum during onstream service.

Hydraulic cutters are used to remove coke from the drum and the first step is to bore a verti-
cal pilot hole through the coke after which cutting heads with horizontally directed nozzles then
undercut the coke and drop it out of the bottom of the drum. Hydraulic pressures in the range of
3000–3600 psi are used in the 26 ft diameter coking drums.

In regard to the process parameters and product yields, an increase in the coking temperature
(1) decreases coke production, (2) increases liquid yield, and (3) increases gas oil end point. On the
other hand, increasing pressure and/or recycle ratio (1) increases gas yield, (2) increases coke yield,
(3) decreases liquid yield, and (4) decreases gas oil end point. As an example, increasing the pres-
sure from the currently designed 15–35 psi (Table 8.6) causes the higher-boiling products to remain
in the hot zone longer causing further decomposition and an increase in yield of the naphtha frac-
tion, a decrease in the yield of the middle distillate–gas oil fraction, and an increase in the yield of
coke.

In the past many delayed coking units were designed to provide complete conversion of atmo-
spheric residue to naphtha, kerosene, and other low-boiling products. However, some units have
been designed to minimize coke and produce heavy coker gas oil (HCGO) that is catalytically
upgraded. The yield slate for a delayed coker can be varied to meet a refiner's objectives through
the selection of operating parameters. Furthermore, delayed coking has an increasingly important
role to play in the integration of modem petroleum refineries because of the inherent flexibility of
the process to handle even the heaviest of residues. The flexibility of operation inherent in delayed
coking permits refiners to process a wide variety of crude oils including those containing heavy,
high-sulfur residua.

Low-pressure coking is a process designed for a once-through, low-pressure operation. The
process is similar to delayed coking except that recycling is not usually practiced and the coke
chamber operating conditions are 435°C (815°F), 25 psi. Excessive coking is inhibited by the
addition of water to the feedstock in order to quench and restrict further reactions of the reactive
intermediates.

High-temperature coking is a semicontinuous process designed to convert asphaltic residua
to gas oil and coke as the primary products. In the process, the feedstock is transported to the
heater (370°C, 700°F, 30 psi) and finally to the coking unit, where temperatures may be as high as
980°C–1095°C (1800°F–2000°F). Volatile materials are fractionated, and after the cycle is com-
plete, coke is collected for sulfur removal before storage.

Delayed coking is likely to remain the workhorse of thermal cracking processes for the foresee-
able future. Online spalling, decoking techniques have been developed, based on successful, similar
application on delayed coker heaters. Heater operation (in delayed coking units and in visbreaker
units) is improved by online spalling of the heater pipes. When an online pipe is to be spalled, flow
is diverted to the offline pipe allowing for full operation of the coker heater. In another embodi-
ment, a thermal transfer resistant zone plate is movably mounted in the radiant section of the coker
heater. By moving the zone plate from an operating position to a spalling position and adjusting the
temperature of the plurality of burners, the temperature of the pipes in the zone of the heater radiant
section to be spalled can be lowered, while the temperature in the remaining zones of the heater
radiant section is fully operational.
Thermal Cracking Processes

The delayed coking process will remain a preferred residue upgrading option because of its ability to handle the heaviest, contaminated crudes. Globally, approximately one-third of installed residue upgrading plant is by delayed coking. Although a mature process, in recent years many developments have taken place, including (1) development of automated coke drum unheeding devices, allowing the operator to carry out the decoking procedure safely from a remote location; (2) understanding of process parameters affecting yields, coker product qualities, and coke qualities (e.g., shot coke); and (3) design and operation of major equipment items, in particular coke drums (allowing shorter coking cycles) and the delayed coker heater (online spalling/decoking and minimization of coking in furnace tubes).

Considering the need for expanding heavy feedstock processing (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014), there will be a need to incorporate operational flexibility into the original design of the delayed coker and make a few key equipment choices with long-term goals in mind. In recent projects and licensing proposals, refineries are also incorporating unique long-term rationales into their designs (Wodnik and Hughes, 2005). For example, some locations intentionally leave plot space and specify design criteria around the coker to allow for easy placement of an additional pair of coke drums with minimal debottlenecking of existing assets. This decision is based upon future plans to construct either another sour crude train or other projects to make more coker feedstock available from existing refinery units. These units utilize the benefit of being online and generating earnings to help pay for the future expansion projects. Incorporating distillate recycle in the processing scheme or at least designing the coker so that recycle technology can be added later at minimal cost is another design strategy possibility.

8.4.2 Fluid Coking

Throughout the history of the refining industry, with only short-term exceptions, there has been a considerable economic driving force for upgrading residua. This has led to the development of processes to reduce residua yields such as thermal cracking, visbreaking, delayed coking, vacuum distillation, and deasphalting. The process is also valuable for conversion of heavy oil, extra heavy oil, and tar sand bitumen to distillates (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). In the process, the hot feedstock is sprayed on to a fluidized bed of hot, fine coke particles, which permits the coking reactions to be conducted at higher temperatures and shorter contact times that can be employed in delayed coking. These conditions result in decreased yields of coke; greater quantities of more valuable liquid product are recovered in the fluid coking process.

As a brief history, in the late 1940s and early 1950s, there was a large incentive to develop a continuous process to convert heavy vacuum residua into lighter, more valuable products. During this period, fluid coking using the principle of fluidized solids was developed and contact coking, using the principle of a moving solid bed, was also developed and the first commercial fluid coker went onstream in late 1954. During the late 1960s, environmental considerations indicated that, in many areas, it would no longer be possible to utilize high-sulfur coke as a boiler fuel. This and other environmental considerations resulted in the development of Flexicoking to convert the coke product from a fluid coker into clean fuel. The first commercial Flexicoking unit went onstream in 1976.

Fluid coking (Figure 8.16) is a continuous process that uses the fluidized solids technique to convert residua, including vacuum residua and cracked residua, to more valuable products (Table 8.9) (Roundtree, 1997). This coking process allows improvement in the yield of distillates by reducing the residence time of the cracked vapors and also allows simplified handling of the coke product. Heat for the process is supplied by partial combustion of the coke with the remaining coke being drawn as product. The new coke is deposited in a thin fresh layer (ca. 0.005 mm, 5 μm) on the outside surface of the circulating coke particle, giving an onion skin effect.
The equipment for the fluid coking process is similar to that used in fluid catalytic cracking (Chapter 9) and follows comparable design concepts except that the fluidized coke solids replace catalyst. Small particles of coke made in the process circulate in a fluidized state between the vessels and are the heat transfer medium and, thus, the process requires no high-temperature preheat furnace.

Fluid coking uses two vessels, a reactor and a burner; coke particles are circulated between these to transfer heat (generated by burning a portion of the coke) to the reactor (Figure 8.16) (Blaser, 1992). The reactor holds a bed of fluidized coke particles, and steam is introduced at the bottom of the reactor to fluidize the bed. The feed coming from the bottom of a vacuum tower at, for example, 260°C–370°C (500°F–700°F) is injected directly into the reactor. The temperature in the coking vessel ranges from 480°C to 565°C (900°F to 1050°F), with short residence times of the order of 15–30 seconds, and the pressure is substantially atmospheric so the incoming feed is partly vaporized and partly deposited on the fluidized coke particles. The material on the particle surface then cracks and vaporizes, leaving a residue that dries to form coke. The vapor products pass through cyclones that remove most of the entrained coke.

Vapor products leave the bed and pass through cyclones that are necessary for removal of the entrained coke. The cyclones discharge the vapor into the bottom of a scrubber and any coke dust remaining after passage through the cyclones is scrubbed out with a pump-around stream and the products are cooled to condense the heavy tar. The resulting slurry is recycled to the reactor. The scrubber overhead vapors are sent to a fractionator where they are separated into wet gas, naphtha, and various gas oil fractions. The wet gas is compressed and further fractionated into the desired components.
### Table 8.9
Examples of Product Yields and Product Properties for Fluid Coking Various Feedstocks

<table>
<thead>
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<th>LA Basin Deasphalter Bottoms</th>
<th>Texas Vacuum Residuum</th>
<th>Kuwait Vacuum Residuum</th>
<th>Louisiana Atmospheric Residuum</th>
<th>Louisiana Vacuum Residuum</th>
<th>Hawkins Vacuum Residuum</th>
<th>Middle East Vacuum Residuum</th>
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<td>API gravity</td>
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<td>Product yields, &lt;sup&gt;b&lt;/sup&gt; vol%</td>
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<td>Naphtha (95°F–425°F; 35°C–220°C)</td>
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<sup>a</sup> Conradson.

<sup>b</sup> A blank product yield line indicates that the yield of the lower-boiling product has been included in the yield of the higher-boiling product.
In the reactor, the coke particles flow down through the vessel into the stripping zone. The stripped coke then flows down a standpipe and through a slide valve that controls the reactor bed level. A riser carries the cold coke to the burner. Air is introduced to the burner to burn part of the coke to provide reactor heat. The hot coke from the burner flows down a standpipe through a slide valve that controls coke flow and thus the reactor bed temperature. A riser carries the hot coke to the top of the reactor bed. Combustion products from the burner bed pass through two stages of cyclones to recover coke fines and return them to the burner bed.

Coke is withdrawn from the burner to keep the solids inventory constant. To aid in keeping the coke from becoming too coarse, large particles are selectively removed as product in a quench elutriator drum and coke fines are returned to the burner. The product coke is quenched with water in the quench elutriator drum and pneumatically transported to storage. A simple jet attrition system in the reactor provides additional seed coke to maintain a constant particle size within the system.

Due to the higher thermal cracking severity used in fluid coking compared to delayed coking, the products are somewhat more olefinic than the products from delayed coking. In general, products are handled for upgrading in a comparable manner from both coking processes. Currently, delayed coking and fluid coking have been the processes of choice for conversion of Athabasca bitumen to liquid products for more than four decades (Figure 8.17) (Speight, 1990, 2000, 2014). Both processes are termed the primary conversion processes for the tar sand plants in Fort McMurray, Alberta, Canada. The unstable liquid product streams are hydrotreated before recombining to the synthetic crude oil.

Coke, being a product of the process, must be withdrawn from the system to keep the solids inventory from increasing. The net coke produced is removed from the burner bed through a quench elutriator drum, where water is added for cooling and cooled coke is withdrawn and sent to storage. During the course of the coking reaction, the particles tend to grow in size. The size of the coke particles remaining in the system is controlled by a grinding system within the reactor.

The coke product from the fluidized process is a laminated sphere with an average particle size of 0.17–0.22 mm (170–220 µm), readily handled by fluid transport techniques. It is much harder and denser than delayed coke, and in general is not as desirable for manufacturing formed products.

The yields of products are determined by the feed properties, the temperature of the fluid bed, and the residence time in the bed. The lower limit on operating temperature is set by the behavior of the fluidized coke particles. If the conversion to coke and light ends is too slow, the coke particles agglomerate in the reactor, a condition known as bogging. The use of a fluidized bed reduces

![Processing sequence for tar sand bitumen.](image-url)
Thermal Cracking Processes

the residence time of the vapor-phase products in comparison to delayed coking, which in turn reduces cracking reactions. The yield of coke is thereby reduced, and the yield of gas oil and olefins increased. An increase of 5°C (9°F) in the operating temperature of the fluid-bed reactor typically increases gas yield by 1% w/w and naphtha by approximately 1% w/w.

The disadvantage of burning the coke to generate process heat is that sulfur from the coke is liberated as sulfur dioxide (SO₂). The gas stream from the coke burner also contains carbon monoxide (CO), carbon dioxide (CO₂), and nitrogen (N₂). An alternate approach is to use a coke gasifier to convert the carbonaceous solids to a mixture of carbon monoxide (CO), carbon dioxide (CO₂), and hydrogen (H₂).

The liquid products from the coker can, following cleanup via commercially available gas oil hydrosulfurization technology (Chapter 10), provide large quantities of low-sulfur fuel (<0.2% by weight sulfur). The incentive for fluid coking or Flexicoking increases relative to alternate processing, such as direct hydroprocessing, as feedstock quality (Conradson carbon, metals, sulfur, nitrogen, etc.) decreases. Changes in yields and product quality result from a change from a low cut point, high reactor temperature operation, to a high cut point operation with a lower reactor temperature (Table 8.10).

Fluid coke is used in electrodes for aluminum manufacture, in silicon carbide manufacture, in ore sintering operations, and as fuel. The coke from a feedstock containing a large amount of contaminants may not be suitable for these uses, either from a product contamination or environmental standpoint. The Flexicoking process overcomes this problem by converting part of the gross coke to a gas that can be burned in process furnaces and boilers. The coke fines from a Flexicoking unit contain most of the metals in the feedstock and may be suitable for metals recovery.

The fluid coking processes can be used to produce a high yield of low-sulfur fuel oil as well as to completely eliminate residual fuel and asphalt from the refinery product slate (Table 8.11). The different distributions are obtained by varying the fluid coker/Flexicoker operating conditions and changing the downstream processing of the coker reactor products. In fact, there are many process variations that can be used to adapt the process to particular refining situations. Once-through or partial recycle coking can be used where there is a small market for heavy fuel oil or where a quantity of high-sulfur material can be blended into the fuel oil pool.

In reference to the process parameters, the reactor temperature is normally set at 510°C–540°C (950°F–1000°F). Low temperature favors high liquid yields and reduces the unsaturation of the gas but increases the reactor holdup requirements. The burner temperature is normally 55°C–110°C (100°F–200°F) above the reactor temperature. Regulating the amount of coke sent to the reactor from the burner controls the reactor temperature. Burner temperature is controlled by the air rate to the burner.

Low pressure provides maximum gas oil recycle cut point, minimizes steam requirements, and reduces air blower horsepower. Reactor pressure normally adjusts to the gas compressor suction pressure but is higher due to the pressure drop through the piping, the condenser, the fractionation tower, and the reactor cyclone. The unit pressure balance required for coke circulation is normally controlled at a fixed differential pressure relative to the reactor sets the burner pressure. Reactor coke level is controlled by the cold coke slide valve on the transfer line from the reactor to the burner and burner coke level is controlled by the coke withdrawal rate.

In all coking processes, product yields are a function of feed properties, the severity of the operation, and recycle cut point (Table 8.12). Severity is a function of time and temperature since low severity and high gas oil cut point favor high liquid yields whereas high severity and low gas oil cut point increase coke and gas yields. Data from these sources indicate that the gross coke yield is directly related to feedstock Conradson carbon residue. Coke quality (Table 8.13) and gas quality (Table 8.14) are also important.

In most cases, high liquid yield and minimum coke and gas yields are required and, in theory, two cracking rates should be considered. The first is the rate at which the liquid cracks and vaporizes after initially laying down on the coke particles that determines the reactor holdup. The second is that vapor-phase cracking determines the distribution of the products between gas, naphtha, and...
The vapor residence time can be determined from the reactor volume and the volume flow of hydrocarbon vapor and steam, and can be divided into time in the fluid bed and time in the disperse phase. The former is a function of the coke holdup or weight space velocity (W/H/W) that is normally expressed as reciprocal hours. For maximum liquid yield, the secondary cracking time should be kept at a minimum and, thus, it is normally desirable to design the unit for the maximum operable W/H/W.

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<th>Feed characteristics</th>
<th>Conradson carbon, wt%</th>
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<td>Gravity, °API</td>
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<tr>
<td></td>
<td>LV below 1000°F, %</td>
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<td></td>
<td>Sulfur, wt%</td>
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<td></td>
<td>Nitrogen, wt%</td>
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<tr>
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</tr>
<tr>
<td></td>
<td>Vanadium, ppm</td>
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<table>
<thead>
<tr>
<th>TABLE 8.10</th>
<th>Flexibility of Operations in Fluid Coking Units Allows Changes to Product Quality</th>
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<tbody>
<tr>
<td>Feed</td>
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<td>Yields</td>
<td>Hydrogen sulfide</td>
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<tr>
<td>Product qualities</td>
<td>C₅ to 215 naphtha</td>
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The maximum rate at which feed can be injected into a fluid coker is limited by a condition known as **bogging**. The conditions required to avoid a bogging are as follows: (1) the feedstock must be uniformly distributed over the entire surface of the heat transfer medium; (2) the layer of feed material on the particles should not be too great; the thickness of the sticky plastic layer depends on the specific flow rate of feedstock, its coking factor, and the recirculation rate of the heat transfer medium; (3) the bed temperature and the initial temperature of the heat transfer medium should be sufficiently high that the first stage of the process is completed in a short time; and (4) the heat transfer medium should not consist of particles that are too fine. The heat reserve of the granules should be sufficient to cover the entire energy requirements in connection with heating the feedstock, supplying the energy for the endothermic cracking reaction, and evaporating the decomposition products. If the

<table>
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<th>Crude Composition</th>
<th>Flexicoking Gas Oil</th>
<th>Hydrodesulfurization</th>
<th>Flexicoking Gas Oil</th>
<th>Hydrodesulfurization and Cat. Cracking</th>
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<td>Sulfur, wt%</td>
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<td>225</td>
<td>1040</td>
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<td>Purge coke, wt%</td>
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feed injection rate exceeds the vaporization rate for an extended period of time, the thickness of the tacky oil film on the particles will increase until the particles rapidly agglomerate, causing the bed to lose fluidity. When fluidization is lost, the heat transfer rate is greatly reduced, further aggravating the condition. Coke circulation cannot be maintained due to the loss of reactor fluidization.

For comparative purposes because of the similarity of the processes, there are some notable differences between the operation of a fluid coker and a fluid catalytic cracking unit (FCCU) and some of these differences tend to make the fluid coker easier to operate. The fluid coker heat balance is very easy to maintain, as there is always an excess of carbon to burn whereas a fluid catalytic cracking unit has a sensitive interaction between heat balance and intensity balance, and therefore between carbon burned and carbon produced, which complicates control, especially during operating changes, start-up, and shutdown.

In addition, recovery from upsets caused by loss of utilities such as steam and air is normally easier and faster with a fluid coker than with a fluid catalytic cracking unit. The fluid coker normally operates well at low feed rates and turndown to low rate is normally limited by the ability of the tower to maintain fractionation of the products. The fluid coker proper can operate at any feed rate that will provide enough coke to heat balance.

However, the fluid coker has some inherent features that can create problems if proper precautions are not followed. The heavy residuum can set up if the lines are not properly heat traced and insulated. Low reactor temperature results in reactor bogging. If the particle size of the circulating coke is not properly controlled, the size can grow to the point that coke circulation problems are encountered. The feed nozzles must be maintained and occasionally cleaned to prevent poor feed distribution followed by excessive agglomerate formation. Control of the reactor bed level is critical.
since an excessively high bed level will flood the reactor cyclone and allow coke to be carried to the scrubber where it will plug the heavy oil circuits.

Along similar lines to the fluid coking process, the *rapid thermal processing* (RTP process, now the HTL process or heavy-to-light upgrading technology) was developed by Ivanhoe Energy Inc. in the 1980s. The process uses a circulating transport bed of hot sand to rapidly induce thermal cracking of the heavy feedstock in the absence of air to produce a light synthetic crude oil (Veith, 2007; Koshka et al., 2008; Silverman et al., 2011).

### 8.4.3 Flexicoking

*Flexicoking* is a direct descendent of fluid coking (Figure 8.16) and uses the same configuration as the fluid coker but includes a gasification section in which excess coke can be gasified to produce refinery fuel gas (Figure 8.18) (Roundtree, 1997; Marano, 2003). The Flexicoking process was designed during the late 1960s and the 1970s as a means by which excess coke could be reduced in view of the gradual incursion of the heavier feedstocks in refinery operations. Such feedstocks are notorious for producing high yields of coke (>15% by weight) in thermal and catalytic operations.

In the process, the heavy feedstock enters the scrubber for direct contact heat exchange with the overhead product vapors from the reactor. The higher-boiling products (>525°C/975°F) present in the overhead condense in the scrubber and return to the reactor as a recycle stream with fresh feedstock. Lower-boiling overhead constituents in the scrubber go to a conventional fractionator and also to light-ends recovery. The feedstock is thermally cracked in the reactor fluidized bed to a range of gas and liquid products, and coke. The coke inventory is maintained by circulating the bed coke from the reactor to the heater via the cold coke transfer line. In the heater, the coke is heated by the gasifier products and circulated back to the reactor via the hot coke transfer line to supply the heat that sustains the thermal cracking process.

![FIGURE 8.18 The Flexicoking process.](image-url)
Excess coke is converted to a low-heating value gas in a fluid-bed gasifier with steam and air. The air is supplied to the gasifier to maintain temperatures of 830°C–1000°C (1525°F–1830°F) but is insufficient to burn all of the coke. The gasifier products, consisting of a gas and coke mixture, return to the heater to heat up the coke. The gas exits the heater overhead and goes to steam generation, to dry/wet particulate removal, and to desulfurization. The clean flexi-gas is then ready for use as fuel in refinery boilers and furnaces and/or for steam and power generation. Approximately 95% w/w of the coke generated in the reactor is converted in the process. Only a small amount of product coke is collected as fines from the flexi-gas and purged from the heater to extract feed metals.

A typical gas product, after removal of hydrogen sulfide, contains carbon monoxide (CO, 18%), carbon dioxide (CO₂, 10%), hydrogen (H₂, 15%), nitrogen (N₂, 51%), water (H₂O, 5%), and methane (CH₄, 1%). The heater is located between the reactor and the gasifier, and it serves to transfer heat between the two vessels. The heater temperature is controlled by the rate of coke circulation between the heater and the gasifier. Adjusting the air rate to the gasifier controls the unit inventory of coke and the gasifier temperature is controlled by steam injection to the gasifier.

Yields of liquid products from Flexicoking are the same as from fluid coking, because the coking reactor is unaltered. The main drawback of gasification is the requirement for a large additional reactor, especially if high conversion of the coke is required. Units are designed to gasify 60%–97% w/w of the coke from the reactor. Even with the gasifier, the product coke will contain more sulfur than the feed, which limits the attractiveness of even the most advance of coking processes.

The Flexicoking process produces a clean fuel gas with a heating value of approximately 90 Btu/ft³ or higher. The coke gasification can be controlled to burn approximately 95% of the coke to maximize production of coke gas or at a reduced level to produce both gas and a coke that has been desulfurized by approximately 65%. This flexibility permits adjustment for coke market conditions over a considerable range of feedstock properties. Fluid coke is currently being used in power plant boilers.

Fluid coking and Flexicoking are versatile processes that are applicable to a wide range of heavy feedstocks and provide a variety of products. The feedstock should have a carbon residue in excess of 5% w/w and there is no upper limit on the carbon residue. Suitable feedstocks include vacuum residua, asphalt, tar sand bitumen, and visbreaker residuum.

### 8.5 OTHER PROCESSES

Typically, in terms of upgrading tar sand bitumen, the bitumen was processed (on the surface) by delayed coking or fluid coking to produce a synthetic crude oil (Figure 8.17) (Speight, 2013, 2014). In a variation of the bitumen upgrading process, bitumen from the separation plant is first sent to an atmospheric distillation tower where the resulting products are naphtha, light gas oil, heavy gas oil, and residue (NRCAN, 2015). Each of the naphtha, light gas oil, and heavy gas oil streams is then sent to its own separate hydrotreater to remove sulfur and nitrogen by adding hydrogen. The resulting products from each of the separate hydrotreaters are then combined to produce synthetic crude oil. The residuum from the atmospheric distillation tower is further separated into two streams, heavy vacuum gas oil and vacuum residue. The heavy vacuum gas oil is mixed with the heavy gas oil from the atmospheric distillation tower to undergo hydrotreating. The vacuum residuum is further upgraded either in a hydroconverter or in a coker to produce lighter liquid product and by-product coke (in the coker). The overhead product from the hydroconverter or coker is further separated into naphtha, light gas oil, and heavy gas oil by distillation. Each of these three streams is mixed with the corresponding liquid product from the atmospheric distillation tower and then sent to the separate hydrotreaters to remove sulfur and nitrogen by adding hydrogen. The final products from the upgrading facility are synthetic crude oil and coke.

The decarbonizing thermal process is designed to minimize coke and gasoline yields but, at the same time, to produce maximum yields of gas oil. The process is essentially the same as the delayed coking process, but lower temperatures and pressures are employed. For example, pressures range from 10 to 25 psi, heater outlet temperatures may be 485°C (905°F), and coke drum temperatures...
may be of the order of 415°C (780°F). Decarbonizing in this sense of the term should not be confused with propane decarbonizing, which is essentially a solvent deasphalting process (Chapter 12).

**Low-pressure coking** is a process designed for a once-through, low-pressure operation. The process is similar to delayed coking except that recycling is not usually practiced and the coke chamber operating conditions are 435°C (815°F), 25 psi. Excessive coking is inhibited by the addition of water to the feedstock in order to quench and restrict the reactions of the reactive intermediates.

**High-temperature coking** is a semicontinuous thermal conversion process designed for high-melting asphaltic residua that yields coke and gas oil as the primary products. The coke may be treated to remove sulfur to produce a low-sulfur coke (≤5%), even though the feedstock contained as much as 5% w/w sulfur. In the process, the feedstock is transported to the pitch accumulator, then to the heater (370°C, 700°F, 30 psi), and finally to the coke oven, where temperatures may be as high as 980°C–1095°C (1800°F–2000°F). Volatile materials are fractionated, and after the cycle is complete, coke is collected for sulfur removal and quenching before storage.

**Mixed-phase cracking** (also called **liquid-phase cracking**) is a continuous thermal decomposition process for the conversion of heavy feedstocks to products boiling in the gasoline range. The process generally employs rapid heating of the feedstock (kerosene, gas oil, reduced crude, or even whole crude), after which it is passed to a reaction chamber and then to a separator where the vapors are cooled. Overhead products from the flash chamber are fractionated to gasoline components and recycle stock, and flash chamber bottoms are withdrawn as a heavy fuel oil. Coke formation, which may be considerable at the process temperatures (400°C–480°C, 750°F–900°F), is minimized by use of pressures in excess of 350 psi.

**Vapor-phase cracking** is a high-temperature (545°C–595°C, 1000°F–1100°F), low-pressure (<50 psi) thermal conversion process that favors dehydrogenation of feedstock (gaseous hydrocarbons to gas oils) components to olefins and aromatics. Coke is often deposited in heater tubes, causing shutdowns. Relatively large reactors are required for these units.

**Selective thermal cracking** is a thermal conversion process that utilizes different conditions depending on the nature of the feedstock. For example, a heavy oil may be cracked at 494°C–515°C (920°F–960°F) and 300–500 psi; a lighter gas oil may be cracked at 510°C–530°C (950°F–990°F) and 500–700 psi (Figure 8.19). Each feedstock has its own particular characteristics that dictate the

**FIGURE 8.19** Selective thermal cracking.
optimum conditions of temperature and pressure for maximum yields of the products. These factors are utilized in selective combination of cracking units in which the more refractory feedstocks are cracked for longer periods of time or at higher temperatures than the less stable feedstocks, which are cracked at lower temperatures.

The process eliminates the accumulation of stable low-boiling material in the recycle stock and also minimizes coke formation from high-temperature cracking of the higher-boiling material. The end result is the production of fairly high yields of gasoline, middle distillates, and olefin gases.

The thermal cracking of naphtha involves the upgrading of low-octane fractions of catalytic naphtha to higher quality material. The process is designed, in fact, to upgrade the heavier portions of naphtha, which contain virgin feedstock, and to remove naphthenes, as well as paraffins. Some heavy aromatics are produced by condensation reactions, and substantial quantities of olefins occur in the product streams.

8.6 OPTIONS FOR HEAVY FEEDSTOCKS

The limitations of processing the more complex difficult-to-convert heavy oil, residua, and tar bitumen depend to a large extent on the amount of nonvolatile higher-molecular-weight constituents, which also contain the majority of the heteroatoms (i.e., nitrogen, oxygen, sulfur, and metals such as nickel and vanadium) (Chapter 1). The chemistry of the thermal reactions of some of these constituents dictates that certain reactions, once initiated, cannot be reversed and proceed to completion and coke is the eventual product (Chapter 3) (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

Upgrading residua, which are similar in character to some heavy oils and tar sand bitumen, began with the introduction of desulfurization processes that were designed to reduce the sulfur content of residua as well as some heavy crude oils and products therefrom. In the early days, the goal was desulfurization but, in later years, the processes were adapted to a 10%–30% partial conversion operation, as intended to achieve desulfurization and obtain low-boiling fractions simultaneously, by increasing severity in operating conditions.

Refinery evolution has seen the introduction of a variety of heavy feedstock cracking processes (some use catalysts and are, of necessity, included here). These processes are different from one another in cracking method, cracked product patterns, and product properties and will be employed in refineries according to their respective features.

8.6.1 Aquaconversion Process

The Aquaconversion process is a hydrovisbreaking technology that uses catalyst-activated transfer of hydrogen from water added to the feedstock. Reactions that lead to coke formation are suppressed and there is no separation of asphaltene-type material (Marzin et al., 1998; Speight and Ozum, 2002; Gary et al., 2007; Speight, 2014). The important aspect of the Aquaconversion technology is that it does not produce any solid by-product such as coke, nor requires any hydrogen source or high-pressure equipment. In addition, the Aquaconversion process can be implanted in the production area, and thus the need for external diluent and its transport over large distances is eliminated.

8.6.2 Asphalt Coking Technology (ASCOT) Process

The ASCOT process (asphalt coking technology process) is a residual oil upgrading process that integrates the delayed coking process and the deep solvent deasphalting process (low energy deasphalting [LEDA]) (Bonilla and Elliot, 1987). Removing the deasphaltered oil fraction prior to application of the delayed coking process has two benefits: (1) in the coking process this fraction is thermally cracked to extinction, degrading this material as an FCC feedstock, and (2) thermally cracking this material to extinction results in conversion of a significant portion to coke.
In the process, the vacuum residuum is brought to the desired extraction temperature and then sent to the extractor where the solvent (straight-run naphtha, coker naphtha) flows upward and extracts soluble material from the down-flowing feedstock. The solvent-deasphalted phase leaves the top of the extractor and flows to the solvent recovery system where the solvent is separated from the deasphalted oil and recycled to the extractor. The deasphalted oil is sent to the delayed coker where it is combined with the heavy coker gas oil from the coker fractionator and sent to the heavy coker gas oil stripper where low-boiling hydrocarbons are stripped off and returned to the fractionator. The stripped deasphalted oil/heavy coker gas oil mixture is removed from the bottom of the stripper and used to provide heat to the naphtha stabilizer–reboiler before being sent to battery limits as a cracking stock. The raffinate phase containing the asphalt and some solvent flows at a controlled rate from the bottom of the extractor and is charged directly to the coking section.

The solvent contained in the asphalt and deasphalted oil is condensed in the fractionator overhead condensers, where it can be recovered and used as lean oil for a propane/butane recovery in the absorber, eliminating the need to recirculate lean oil from the naphtha stabilizer. The solvent introduced in the coker heater and coke drums results in a significant reduction in the partial pressure of asphalt feed, compared with a regular delayed coking unit. The low asphalt partial pressure results in low coke and high liquid yields in the coking reaction.

With the ASCOT process, there is a significant reduction in by-product fuel as compared to either solvent deasphalting or delayed coking and the process can be tailored to process a specific quantity or process to a specific quality of cracking stock (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

### 8.6.3 Cherry-P Process

The Cherry-P process (comprehensive heavy ends reforming refinery process) is a process for the conversion of heavy crude oil or residuum into distillate and a cracked residuum. In this process, the principal aim is to upgrade heavy petroleum residues at conditions between those of conventional visbreaking and delayed coking. Although coal is added to the feedstock, it is not intended to be a coprocessing feedstock but the coal is intended to act as a scavenger to prevent the buildup of coke on the reactor wall. The use of scavengers in the process is projected to increase (Stark and Falkler, 2008; Stark et al., 2008; Speight, 2014).

In the process, the feedstock is mixed with coal powder in a slurry mixing vessel (without a catalyst or hydrogen), heated in the furnace, and fed to the reactor where the feedstock undergoes thermal cracking reactions for several hours at a temperature higher than 400°C–450°C (750°F–840°F) and under pressure (70–290 psi) with a residence time on the order of 1–5 hours. Gas and distillate from the reactor are sent to a fractionator and the cracked residuum is extracted out of the system after distilling low-boiling fractions by the flash drum and vacuum flasher to adjust its softening point. Distillable product yields of 44% by weight on total feed are reported (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). Since this yield is obtained when using anthracite, the proportion that is derived from the coal is likely to be very low and unlikely to cause compatibility reactions in downstream reactors due to the presence of phenols and other polar species (Speight, 1990, 2014).

### 8.6.4 Continuous Coking Process

A new coking process that can accept heavy feedstock and continuously discharge vapor and dry petroleum coke particles has been developed (Sullivan, 2011). The process promotes a rapid recovery of volatiles from the resid enabling recovery of more volatiles. It also causes the carbonization reactions to proceed more rapidly, and it produces uniform composition and uniform size of coke particles that have a low volatiles content.

The new process uses a kneading and mixing action to continuously expose new resid surface to the vapor space and causes a more complete removal of volatiles from the produced
petroleum coke. Not only are more valuable volatiles recovered, the volatiles are likely to be richer in middle distillates. As a result of kneading/mixing action by the reactor/devolatilizer, new surfaces of the residuum mass are continuously exposed to the gas phase, enhancing the rapid mass transfer of volatiles into the gas phase. The volatiles are then rapidly cooled to retard degradation. With the rapid reduction of volatiles content in the resid mass, the carbonization reaction rates are accelerated, enabling continuous and rapid production of solid petroleum coke particles. The short contact time of the volatiles with the hot residuum minimizes thermal degradation of volatiles.

Concurrently with the carbonization reactions and the formation of coke, some cracking of side chains off the larger molecules likely occurs. These smaller, low-boiling molecules produced from cracking reactions join the population of the indigenous volatiles. Some volatiles may be generated even after the solid coke is formed. In the delayed coking process, many of these late forming volatiles remain trapped in the coke. The process promotes the release of these late forming cracked volatiles, allowing them to escape into the gas phase by breaking the solid coke into small particles.

In addition to the recovery of additional and more valuable volatiles, there are other benefits of the new process compared to the delayed coking process. The consumption of utilities is less because no steam or water is required. Since there is no quenching, energy from the hot coke is recovered. The process is continuous so is never opened to the atmosphere. There is no cutting procedure as in the delayed coking process where high-pressure water is used to cut the coke out of the drums. Therefore, no volatiles and no coke particles are released into the atmosphere.

### 8.6.5 Decarbonizing Process

The thermal decarbonizing process (not to be confused with the propane decarbonizing process, which is a deasphalting process) is designed to minimize coke and gasoline yields but, at the same time, to produce maximum yields of gas oil. Decarbonizing in this sense of the term should not be confused with propane decarbonizing, which is essentially a solvent deasphalting process (Speight and Ozum, 2002; Hsu and Robinson, 2006; Speight, 2014). Thermal decarbonizing is, in many respects, similar to the delayed coking process, but lower temperatures and pressures are employed. For example, heater outlet temperatures may be 485°C (905°F) and coke drum temperatures may be of the order of 415°C (780°F) while pressures range from 10 to 25 psi.

### 8.6.6 ET-II Process

The ET-II process is a thermal cracking process for the production of distillates and cracked residuum for use as metallurgical coke and is designed to accommodate feedstocks such as heavy oils, atmospheric residua, and vacuum residua (Kuwahara, 1987). The distillate (cracked oil) is suitable as a feedstock to hydrocracker and fluid catalytic cracking. The basic technology of the ET-II process is derived from that of the original Eureka process.

In the process, the feedstock is heated up to 350°C (660°F) by passage through the preheater and fed into the bottom of the fractionator, where it is mixed with recycle oil, and the high-boiling fraction of the cracked oil. The ratio of recycle oil to feedstock is within the range of 0.1%–0.3% by weight. The feedstock mixed with recycle oil is then pumped out and fed into the cracking heater, where the temperature is raised to approximately 490°C–495°C (915°F–925°F), and the outflow is fed to the stirred-tank reactor where it is subjected to further thermal cracking. Both cracking and condensation reactions take place in the reactor.

The cracked oil and gas products, together with steam from the top of the reactor, are introduced into the fractionator where the oil is separated into two fractions, cracked light oil and vacuum gas oil, and pitch (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).
8.6.7 **Eureka Process**

The Eureka process is a thermal cracking process to produce a cracked oil and aromatic residuum from heavy residual materials (Aiba et al., 1981; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Ohba et al., 2008; AlHumaidan et al., 2013a,b; Speight, 2014). The cracking reactions occur under lower cracked oil partial pressure by introducing steam into the reactor. The unconverted cracked residuum (pitch) in the reactor behaves as a homogeneous system that provides stable and trouble-free operating conditions. The cracked oil is further hydrotreated, cracked, and/or hydrocracked to produce marketable fuels, and the cracked residuum is utilized as a boiler fuel or as a gasification (partial oxidation) feedstock for hydrogen production or synthesis gas production (Chapter 14).

In this process (Figure 8.20), the heavy feedstock is fed to the preheater and then enters the bottom of the fractionator, where it is mixed with the recycle oil. The mixture is then fed to the reactor system that consists of a pair of reactors operating alternately. In the reactor, thermal cracking reaction occurs in the presence of superheated steam which is injected to strip the cracked products out of the reactor and supply a part of heat required for cracking reaction. At the end of the reaction, the bottom product is quenched. The oil and gas products (and steam) pass from the top of the reactor to the lower section of the fractionator, where a small amount of entrained material is removed by a wash operation. The upper section is an ordinary fractionator, where the heavier fraction of cracked oil is drawn as a side stream. The process bottoms (pitch) can be used as boiler fuel, as partial oxidation feedstock for producing hydrogen and carbon monoxide, and as binder pitch for manufacturing metallurgical coke (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

The process reactions proceed at lower cracked oil partial pressure by injecting steam into the reactor, keeping petroleum pitch in a homogeneous liquid state and, unlike a conventional delayed coker, a higher cracked oil yield can be obtained. A wide range of residua can be used as feedstock, such as atmospheric and vacuum residue of petroleum crude oils, various cracked residues, asphalt products from solvent deasphalting and native asphalt. After hydrotreating, the cracked oil is used as feedstock for a fluid catalytic cracker or hydrocracker.

The original Eureka process uses two batch reactors, while the newer ET-II and the HSC process both employ continuous reactors.

![FIGURE 8.20 The Eureka process.](image-url)
8.6.8 FTC Process

The FTC process (fluid thermal cracking process) is a heavy oil and residuum upgrading process in which the feedstock is thermally cracked to produce distillate and coke (Miyauchi et al., 1981, 1987; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

The feedstock, mixed with recycle stock from the fractionator, is injected into the cracker and is immediately absorbed into the pores of the particles by capillary force where it is subjected to thermal cracking. In consequence, the surface of the noncatalytic particles is kept dry and good fluidity is maintained allowing a good yield of, and selectivity for, middle distillate products. Hydrogen-containing gas from the fractionator is used for the fluidization in the cracker. Excessive coke caused by the metals accumulated on the particle is suppressed under the presence of hydrogen. The particles with deposited coke from the cracker are sent to the gasifier, where the coke is gasified and converted into carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), and hydrogen sulfide (H₂S) with steam and air. Regenerated hot particles are returned to the cracker.

8.6.9 HSC Process

The HSC process (high conversion soaker cracking process) is a cracking process designed for moderate conversion, higher than visbreaking but lower than coking (Watari et al., 1987; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). The process is an advanced continuous thermal cracking technology with a proprietary soaking drum, featuring a wide range of conversion levels between visbreaking and coking while producing pumpable liquid residue at process temperature. A broad range of heavy feedstocks such as heavy crude, long and short residue with high contents of sulfur and heavy metals and even visbroken residue can be charged to the HSC process. The cracked distillates from the HSC process are mostly light and heavy gas oils with fewer unsaturated compounds than coker distillates. The heavy gas oil fraction serves as the feedstock to the fluid catalytic cracking unit and the cracked residue can be used as the fuel for boiler at the power station. The process uses no hydrogen, no catalyst, and no high-pressure equipment. The process economics is benefited by low investment cost and low utilities consumptions due to its simple process scheme as visbreaking process. The process features less gas make and a higher yield of distillate compared to other thermal cracking processes. The process can be used to convert a wide range of feedstocks with high sulfur and metal content, including heavy oils, oil sand bitumen, residua, and visbroked residua. As a note of interest, the HSC process employs continuous reactors whereas the original Eureka process (q.v.) uses two batch reactors.

In the process, the preheated feedstock enters the bottom of the fractionator, where it is mixed with the recycle oil. The mixture is pumped up to the charge heater and fed to the soaking drum (ca. atmospheric pressure, steam injection at the top and bottom), where sufficient residence time is provided to complete the thermal cracking. In the soaking drum, the feedstock and some product flows downward passing through a number of perforated plates while steam with cracked gas and distillate vapors flows through the perforated plates countercurrently.

The volatile products from the soaking drum enter the fractionator where the distillates are fractionated into desired product oil streams, including a heavy gas oil fraction. The cracked gas product is compressed and used as refinery fuel gas after sweetening. The cracked oil product after hydrotreating is used as fluid catalytic cracking or hydrocracker feedstock. The residuum is suitable for use as boiler fuel, road asphalt, binder for the coking industry, and as a feedstock for partial oxidation.

8.6.10 Mixed-Phase Cracking Process

The mixed-phase cracking process (also called liquid-phase cracking) is a continuous thermal decomposition process for the conversion of heavy feedstocks to products boiling in the gasoline range. The process generally employs rapid heating of the feedstock (kerosene, gas oil, reduced
crude, or even whole crude), after which it is passed to a reaction chamber and then to a separator where the vapors are cooled. Overhead products from the flash chamber are fractionated to gasoline components and recycle stock, and flash chamber bottoms are withdrawn as a heavy fuel oil. Coke formation, which may be considerable at the process temperatures (400°C–480°C, 750°F–900°F), is minimized by use of pressures in excess of 350 psi.

**8.6.11 SELECTIVE CRACKING PROCESS**

*Selective cracking* is a thermal conversion process that utilizes different conditions depending on feedstock composition. For example, a heavy oil may be cracked at 494°C–515°C (920°F–960°F) and 300–500 psi; a lighter gas oil may be cracked at 510°C–530°C (950°F–990°F) and 500–700 psi (Moschopedis et al., 1998; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014).

Each feedstock has its own particular characteristics that dictate the optimum conditions of temperature and pressure for maximum yields of the products. These factors are utilized in selective combination of cracking units in which the more refractory feedstocks are cracked for longer periods of time or at higher temperatures than the less stable feedstocks, which are cracked at lower temperatures.

The process eliminates the accumulation of stable low-boiling material in the recycle stock and also minimizes coke formation from high-temperature cracking of the higher-boiling material. The end result is the production of fairly high yields of gasoline, middle distillates, and olefin gases.

**8.6.12 SHELL THERMAL CRACKING PROCESS**

The Shell thermal distillate cracking unit is based on the principle of converting high-boiling feedstocks to lower-boiling products (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). Thermal cracking of heavy oil takes place in the liquid phase in a furnace, at elevated pressure and temperature and the products are residuum and distillate products.

In the process, the feedstock (e.g., heavy gas oils from the atmospheric distillation unit or vacuum gas oil from the vacuum distillation unit) is sent to a surge drum. Liquid from this drum is pumped to the distillate heater, which typically operates at a pressure of approximately 490°C (915°C) and 290 psi. Under these conditions, the cracking reactions take place in the liquid phase.

Fluid from the distillate heater is then routed to the combi tower where separation is achieved between residue, gas oil, and lighter products. In addition, a heavy gas oil fraction is taken from the combi tower, returned to the surge drum, and then recycled through the distillate heater. The bottom product of the combi tower is routed to a vacuum flasher where heavy gas oil is recovered from the residuum stream and routed back to the distillate heater. The vacuum flashed residuum from the vacuum flasher can be routed to fuel oil blending or can be used internally as refinery fuel. The recycling of heavy gas oil from both the vacuum flasher and the combi tower to the distillate heater means that all of the heavy gas oil is converted. Light gas oil from the combi tower is first stripped and is then routed to a hydrotreater. Alternatively, the light gas oil can be used as cutter stock.

The feedstock and product requirements of the thermal distillate cracking process are flexible, and the process has the capability to optimize conversion through adjustment of the heavy gas oil recycle rate.

The *Shell deep thermal gasoil process* is a combination of the *Shell deep thermal conversion process* and the *Shell thermal gasoil process*. In this alternative high conversion scheme, the heavy gas oil (HGO) from the atmospheric distillation unit and the vacuum gas oil (VGO) from the vacuum flasher or vacuum distillation unit are cracked in a distillate thermal cracking heater into lower-boiling range gasoil.

A related process, the *deep thermal conversion process* (DTC process) (Figure 8.21) offers a bridge between visbreaking and coking and provides maximum distillate yields by applying deep
thermal conversion to vacuum residua followed by vacuum flashing of the products. In the process, the heated vacuum residuum is charged to the heater and from there to the soaker where conversion occurs. The products are then led to an atmospheric fractionator to produce gases, naphtha, kerosene, and gas oil. The fractionator residuum is sent to a vacuum flasher that recovers additional gas oil and distillate. The next steps for the coke are dependent on its potential use and it may be isolated as liquid coke (pitch, cracked residuum) or solid coke. The process yields a maximum of distillates from heavy feedstocks (such as vacuum residua) and by vacuum flashing the cracked residue. The liquid coke, not suitable for blending to commercial fuel, is used for specialty products, gasification and/or combustion, for example, to generate power and/or hydrogen.

### 8.6.13 TervaHl-T Process

The TervaHl-T process offers options that allow the process to accommodate differences in the feedstock as well as the desired sale of products. In the process (Peries et al., 1988; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014), the feedstock is heated to the desired temperature using the coil heater and heat recovered in the stabilization section and held for a specified residence time in the soaking drum. The soaking drum effluent is quenched and sent to a conventional stabilizer or fractionator where the products are separated into the desired streams (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014). The gas produced from the process is used for fuel.

In the related TervaHl-H process (a hydrogenation process but covered here for convenient comparison with the TervaHl-T process), the feedstock and hydrogen-rich stream are heated using heat recovery techniques and fired heater and held in the soak drum as in the TervaHl-T process. The gas and oil from the soaking drum effluent are mixed with recycle hydrogen and separated in the hot separator where the gas is cooled and passed through a separator and recycled to the heater and soaking drum effluent. The liquids from the hot and cold separator are sent to the stabilizer section where purge gas and synthetic crude are separated. The gas is used as fuel and the synthetic crude can now be transported or stored.
REFERENCES


