3

Downstream Processing of Heavier Petroleum Fractions

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ABSTRACT This chapter focuses on different processes for upgrading the heavy petroleum residues into valuable products. It highlights the growing demand for petroleum products every year and diminishing supplies of crude oil. It enlists the essential properties of these residues and provides the much needed selection criteria for adopting an upgradation technique. It discusses various upgradation techniques, that is, visbreaking, delayed coking, hydrocracking, and so on, and recent advancements that have been incorporated into them. It examines the merits and demerits of these techniques and compares them. It gives an overview of the biotechnological processes for the residue utilization.

3.1 Introduction

In a typical refinery, after desalting and atmospheric distillation, the petroleum crude is converted into petroleum gas, light and heavy naphtha, gasoline, kerosene, jet fuel, diesel oil, atmospheric gas oil, and atmospheric bottoms. The residue from the atmospheric distillation column (atmospheric bottoms) is further processed in a vacuum distillation column to produce light and heavy vacuum gas oil (VGO) as well as vacuum residue (VR). The heavier fractions such as VR, VGO, and atmospheric gas oil, further go through a
number of catalytic and noncatalytic downstream processing steps to produce valuable products as well as to meet the market demand (Marafi et al. 2010). Gradual increase in sulfur and metal contents of petroleum crude as well as its viscosity make it heavier and difficult for processing through the conventional refinery unit. It produces higher amount of heavier fractions containing more metals and sulfur than light crude oil. The typical concentrations of sulfur, nitrogen, and metals (V and Ni) in light as well as heavy crude oils are provided in Table 3.1.

Therefore, the upgradation of heavier fractions through downstream processing is becoming more interesting day by day and attracting attention of refiners. It has also been reported that for utilizing heavy and extra heavy crude oils, refining and nonrefining processes need to be integrated (Marafi et al. 2010). Based on the work of Rana et al. (2008), a suitable flowsheet for heavy and extra heavy petroleum crudes is shown in Figure 3.1. From the figure, it seems that a part of heavy and extra heavy crude oils avoids the distillation step and is processed through conventional downstream processing steps.

### Table 3.1

<table>
<thead>
<tr>
<th>Property</th>
<th>Light Crude Oil</th>
<th>Heavy Crude Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (wt.%)</td>
<td>0.1</td>
<td>Up to 1</td>
</tr>
<tr>
<td>Sulphur (wt.%)</td>
<td>0.05</td>
<td>Up to 5</td>
</tr>
<tr>
<td>Metals (ppm)</td>
<td>~3</td>
<td>Up to ~600</td>
</tr>
</tbody>
</table>

Heavy crude oil is thicker with an American Petroleum Institute (API) gravity of less than 20°, more resistant to flow, and usually contains higher levels of sulfur and other contaminants than light crude oil. It gives more residues after the processing of crude oil from the vacuum distillation unit than light crude oil. According to the density, heavy crudes can be classified as heavy oils (API within 10°–20°) and extra heavy oils (API < 10°) (Manning and Thompson 1995). The in situ viscosity makes the distinction between extra heavy oils and bitumen. It is reported that during the past 15 years (2001–2015), the demand for petroleum products has grown with a rate of ~1.7% per annum, which is also expected to continue over the next 15 years (Hedrick and Seibert 2006)(Web 1). Further, the supplies of light crudes have diminished in recent years, whereas global heavy oil consumption is increasing gradually, and it is predicted to continue until 2030 (World Energy Outlook 2008). Therefore, both the heavy crude oil containing 40%–64% residues and the nondistillable heavy residues produced from it attract strong interest from the refiners to produce valuable products (Speight 2000; Marafi et al. 2010).

In addition, the market demand for different petroleum products varies with time, for example, in recent years middle distillates have been in more demand, whereas in the past (until 2007), gasoline was in higher demand (U.S.A. Energy Information Administration 2016). In the present scenario, conversion of heavy residues into light-value products and subsequent processing are more attractive than its conventional use as a heavy fuel component (Sarkar 1998). Many methods including high vacuum distillation, shortcut distillation (cutpoint extended up to 700°C), and sequential extraction fractionation have been developed for the fractionation of heavy crude oils (Chung et al. 1997). Some upgradation techniques such as thermal cracking, catalytic cracking, hydrocracking (HDC), and solvent extraction are also applied for processing heavy petroleum crudes as well as heavy residues generated by the fractionation. Figure 3.2 shows the contribution of different processes such as cracking/visbreaking, coking, HDC, hydrotreating (HDT), and deasphalting to the downstream processing of heavy residues.

For the upgradation of different types of gas oils (atmospheric, light vacuum, and heavy vacuum), generally hydrogen addition processes (HDT, HDC, etc.) are used, whereas for
processing vacuum residues, carbon rejection processes (thermal and catalytic cracking) are preferred. Thermal cracking may be visbreaking and delayed coking. Selection of a suitable process for the upgradation of residue depends upon the carbon residue and the metal content in the residue. As shown in Figure 3.3, residues having lower Conradson Carbon Residue (CCR) and metal content (<6% and 15 ppm, respectively) are suitable for catalytic cracking, whereas residues having higher carbon residue and metal content (>10% and 150 ppm, respectively) are suitable for carbon rejection.

A little heavier feedstock (CCR ≤ 10%) containing a metal content of ≤150 ppm can be processed through hydroprocessing. Some important technologies used in this process are Shell’s hydroconversion (HYCON) and Chevron’s on-stream catalyst replacement (OCR). Hydroprocessing has some advantages over catalytic cracking as it can handle relatively heavier feedstocks with more heavy metal content, and it can also produce good-quality products such as catalytic cracking. However, its processing/investment cost and the need for hydrogen limit its application for the feedstocks having a CCR value and a metal content of more than 10% and 150 ppm respectively, which can be upgraded through non catalytic carbon rejection process (Shen et al. 1998; Phillips and Liu 2002).

Heavy petroleum crude has higher impurities content, and it yields lower middle distillates, which have a high market demand. It also produces heavier residues due to the presence of more paraffins, naphthenes as well as aromatics, including asphaltenes and resins. The properties of heavy residues depend on the constituents of crude oil and are important to select/develop suitable upgradation processes because the chemical structure and complexity of the residues influence the upgradation process.

### 3.1.1 Properties of Heavy Petroleum Residues

A residual oil is composed of asphaltenes, resins, aromatics, and saturated hydrocarbons as shown in Figure 3.4 (Chrisman et al. 2012).
It can be described as a colloidal system in which the dispersed phase comprises asphaltenes and the continuous phase represents maltene/oil (containing aromatics, resins, and saturated hydrocarbons). The resin molecules play the role of surfactants in stabilizing colloidal particles of asphaltenes in oil. During thermal cracking, the oil phase cracks, and after certain limit of cracking, the colloidal equilibrium is disturbed, which results in flocculation of asphaltenes. At this stage, cracked fuel oil becomes unstable in nature (Hur et al. 2014). Heavy residues contain higher viscosity, heavy metals, sulfur, nitrogen, and naphthenic acids. Some important physicochemical characteristics of VR are provided in Table 3.2.

Asphaltenes correspond to a crude oil fraction consisting of polar molecules having high molecular weight, which are capable of self-association at a critical concentration. The VR is also rich in aromatic content normally in the CCR range of 15–25 wt.%. In some cases, the CCR value is less (1%–6%), where naphthene quantity becomes more (Schulman and Dickenson 1991). The aromatic content influences the viscosity, and the coupling of viscosity with CCR helps to evaluate the average molecular weight of the feedstocks, which is related to the kinematic viscosity. The higher the aromaticity of a heavy oil, the higher is its viscosity (Speight 1991). Because the asphaltenes are the most viscous aromatic compounds in a heavy oil, their influence on the heavy oil viscosity is maximum among all other heavy oil constituents. The converted vacuum residual oils (from visbreaking and residue ebullated bed H-Oil HDC unit) demonstrate the lower dependence of viscosity on the asphaltene content. This could be a result of decreasing dimensions in the macrostructure of the converted asphaltene molecule. The mass ratio of asphaltenes and resins in a heavy residue influences its stability, whereas its surface properties are dependent on the association of nonpolar and polar constituents as well as their molecular composition. Asphaltene has a high molecular weight and is insoluble in n-pentane and other noncyclic hydrocarbons. It is nonvolatile and held in colloidal suspension in the hydrocarbon phase with the resins, which act as peptizing agents. Different tests such as merit number test (IFP-3024-82), Shell P-value test (1400-2), toluene/xylene equivalent test, and Shell hot filtration test (SMS 742) are used to determine the stability of a heavy residue.

**TABLE 3.2**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 135°C (cSt)</td>
<td>2.0E+02</td>
<td>Jechura 2016 (Web 5)</td>
</tr>
<tr>
<td>Gravity, API</td>
<td>10.0°</td>
<td></td>
</tr>
<tr>
<td>Heating value (kcal/kg)</td>
<td>10310</td>
<td></td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>615</td>
<td>Altgelt and Boduszynski (1994)</td>
</tr>
<tr>
<td>H/C ratio</td>
<td>~1.38</td>
<td>Furimsky (1999)</td>
</tr>
<tr>
<td>Heavy metals (wt.%)</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Elemental carbon (wt.%)</td>
<td>79.75</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (wt.%)</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Sulphur (wt.%)</td>
<td>4.20</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Upgradation of Heavy Residues

Carbon rejection and hydrogen addition are the two types of processes used for the upgradation of heavy residues. Visbreaking, fluid catalytic cracking (FCC), steam cracking, delayed coking, and solvent extraction methods are the important conventional carbon rejection processes, whereas fixed bed and ebullated bed catalytic hydroconversion, HDC, hydrovisbreaking, and donor solvent processes are the important conventional hydrogen addition processes. Application of nanomaterials, gasification, and biological processes are some emerging technologies for the processing of heavy residues. The hydroconversion processes are mostly catalytic, whereas the carbon rejection processes may be catalytic or noncatalytic. In case of the solvent extraction method, some solvents are required to separate the asphaltenes and resins from the heavy residue. Hydrogen addition processes have higher product flexibility and produce good-quality products, although these are costlier than carbon rejection methods. In terms of the operating cost and simplicity, the noncatalytic carbon rejection processes are superior to others and have been widely used for the upgradation of heavy residues around the world. Delayed coking and visbreaking processes account for approximately 63% of the value addition processes of heavy residues (Sawarkar et al. 2007). Thermal cracking of heavy residue is an old process; however, due to its complex nature and nonavailability of analytical facilities, the kinetic modeling of this process was not explored initially. Some important residue upgradation processes are described in Sections 3.2.1 through 3.2.7.

3.2.1 Visbreaking

Visbreaking process has been developed to produce fuel oil from heavy residue to save the valuable lighter products called “cutter stocks.” Today, visbreaking units are also used to prepare the feedstocks for secondary units such as FCC and hydrocracker. This process reduces the viscosity of petroleum residue due to heat application and also produces a small amount of light hydrocarbons such as liquefied petroleum gas (LPG), naphtha, and gasoline, heavy gas oil, and residual part with reduced viscosity.

A typical visbreaking unit consists of a furnace reactor, a flash chamber, and a fractionating column. The furnace is normally coil type, and the typical operating conditions for furnace are as follows:

- Furnace inlet temperature 305°C–325°C and pressure 15–40 bar
- Furnace outlet temperature 480°C–500°C and pressure 2–10 bar
- Residence time 2–5 min
- Steam injection 1 vol.%

To reduce the furnace temperature, a soaker unit is placed between the flash chamber/fractionator and the furnace as shown in Figure 3.5. Temperature and pressure maintained in the soaker unit are 440°C–460°C and 5–15 bar with a residence time of 20–30 min, respectively. Preheating of the feedstock to ~335°C is done by using visbreaking tar. The overhead product of the flash chamber gives naphtha, LPG, and gasoline, and the bottom liquid is further fractionated into gas oil and residual product (reduced viscosity). In this
process, approximately fivefold viscosity reduction is possible when 5%–10% naphtha is produced. It is a complex process and the reaction mechanism for the production of light hydrocarbons can be expressed through a typical free radical mechanism (Equations 3.1 through 3.10):

Initiation

\[ C_6H_{14} \rightarrow C_2H_5\cdot + C_4H_9\cdot \]  (3.1)

Propagation

\[ C_2H_5\cdot + C_6H_{14} \rightarrow C_2H_6 + C_6H_{13}\cdot \]  (3.2)

\[ C_4H_9\cdot + C_6H_{14} \rightarrow C_4H_{10} + C_6H_{13}\cdot \]  (3.3)

Radical \( C_6H_5\cdot \) can be cracked to different species as per the following equations, as big radicals are unstable and decomposed to form olefins and smaller radicals.

\[ C_4H_9\cdot \rightarrow C_4H_8 + H\cdot \]  (3.4)

\[ C_4H_9\cdot \rightarrow C_3H_6 + CH_3\cdot \]  (3.5)

\[ C_4H_9\cdot \rightarrow C_2H_4 + C_2H_5\cdot \]  (3.6)

Radical \( C_6H_{13}\cdot \) may further be cracked as per the following equation:

\[ C_6H_{13}\cdot \rightarrow C_4H_8 + C_2H_5\cdot + \text{many other products} \]  (3.7)
Termination

The free radical chain reaction is terminated when the radicals combine:

\[ \text{C}_2\text{H}_5\bullet + \text{H}\bullet \longrightarrow \text{C}_2\text{H}_6 \]  
(3.8)

\[ \text{C}_2\text{H}_5\bullet + \text{CH}_3\bullet \longrightarrow \text{C}_3\text{H}_8 \]  
(3.9)

\[ \text{CH}_3\bullet + \text{H}\bullet \longrightarrow \text{CH}_4 \]  
(3.10)

Visbreaking can produce a visbroken product with lower viscosity and pour point. Depending upon the reactor design, this process can be classified into two categories: soaker visbreaking and coil visbreaking.

The soaker visbreaking process as shown in Figure 3.5 is a relatively low-temperature process with a relatively high-residence time (100–300 s for coil visbreaker and 1200–1800 s for soaker visbreaker). In this case, a two-stage conversion, a minor degree of conversion for a short period in the furnace and a major degree of conversion for a predetermined extended period in the soaker unit, takes place. The low-temperature operation saves fuel consumption; however, decoking in the soaker unit requires more equipment and handling cost. It also generates more wastewater as high-pressure water is used for decoking in the soaker unit. In the coil visbreaking unit, the furnace itself contains a dedicated soaker in which most cracking takes place. The cracked products from the furnace outlet are quenched by preheating the furnace feed or heating cold gas oil, which helps to cease cracking reactions. The quenched products yield LPG, gasoline, gas oil, and tar in the fractionator. The speed of the feedstock in the tubes of the furnace controls the extent of cracking reaction. Decoking is frequent but easy for coil-type visbreakers. In terms of the product yield, there is little difference between the two reactor options (soaker visbreaker and coil visbreaker). Fouling in the soaker unit is slower than in the tubes of the furnace, but it increases the downtime of the whole unit. Recently, improvement in heater design has been able to eliminate the downtime of coil visbreaking (Speight 2012). Similarly, the application of internals in the soaker visbreaker is an important development, which controls the back-mixing in the soaker unit. Back-mixing can enhance overcracking, which reduces the stability of fuel oil and can be avoided if radial gas holdup profile is flat. The application of soaker internals satisfies this condition and controls the stability of products. It also increases conversion, reduces heat duty, and enhances run length by preventing undesirable side reactions leading to coke formation. Table 3.3 shows the comparison of conversion and viscosity of the cracked products obtained from the soaker with and without internals using the VR from Arab Mix Short Residue–Hindustan Petroleum Corporation Limited, Mumbai, India (Kumar et al. 2004).

In the visbreaking process, feedstock composition (properties) as well as the operating parameters influence the product yields and specifications. Decomposition of

<table>
<thead>
<tr>
<th>TABLE 3.3</th>
<th>Comparison of Performances of Internals in the Soaker Unit</th>
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<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Conversion at 150°C (wt.%)</td>
</tr>
<tr>
<td>Soaker without internals</td>
<td>420</td>
</tr>
<tr>
<td>Soaker with internals</td>
<td>420</td>
</tr>
</tbody>
</table>

different types of compounds present in the feedstock varies as follows: \( n \)-paraffins > \( i \)-paraffins > cycloparaffins > aromatics > aromatic–naphthanes > polynuclear aromatics. Heavy hydrocarbon oils and resins can easily crack thermally, but it is difficult to crack asphaltenes. First, they are partially cracked into lighter products, and then carboids and coke are formed through polymerization, condensation, dehydrogenation, and dealkylation reactions. The carboids and coke as well as asphaltenes remain in stable colloidal suspension unless visbreaking reactions proceed too far. After certain limit of visbreaking, they tend to precipitate from the oil and form deposits in the cracking furnace and produce unstable fuel oil (Kuo 1985).

An increase in temperature at constant pressure and conversion increases the amount of lighter material in the products and decreases the yield of heavy oil and coke (Safiri et al. 2015). The properties of cracked gasoline also change with temperature as unsaturates increase gradually with an increase in temperature.

With increase in cracking time, the gasoline fraction gradually increases, reaches a maximum value, and decreases thereafter because of secondary reactions converting some gasoline into smaller hydrocarbon as well as polymerization of gasoline to some higher molecules. Extended cracking time produces more saturates in products. An increase in pressure enhances the polymerization of light unsaturates in the vapor phase and yields more liquid products.

Although visbreaking reduces the viscosity, it reaches a limiting value with an increase in conversion, and hence, addition of diluent is required if the cracked product is required to be transported through pipelines. Further, the products of visbreaking are not stable due to the presence of unsaturated molecules. In spite of this disadvantage, this method is widely used for the upgradation of heavy residues around the world.

### 3.2.2 Delayed Coking

In the delayed coking process, the coke formation is obtained by providing a sufficient long residence time (delayed) in the coke drum. More lighters are obtained and coke is obtained as a by-product. Delayed coking consists of thermal cracking of heavy residue in the empty drum in which deposition of coke takes place. The product yield and quality depends on the type of feedstock processed. A typical delayed coking consists of a furnace to preheat the feed, a coking drum in which cracking and coke formation take place, and a downstream fractionator of the coke drum in which the fractionation of the vapor-phase products take place. A process flow diagram for delayed coking is shown in Figure 3.6. The feed is first preheated in the furnace in which the desired cooking temperature (around 490°C–510°C) is achieved and fed to the coking drums, which are maintained at a pre-fixed temperature and are normally installed in pairs where the cracking reaction takes place and the coke is deposited at the bottom of the drum. The pressure of the coke drum gradually builds up, and after attaining a required pressure (~3 kg/cm²), the coke drum overhead vapor is allowed to flow into the fractionating column in which it is separated into overhead streams containing wet gas, LPG, and naphtha as well as two-side gas oil streams. Recycled stream from the fractionating column combines with the fresh feed in the bottom of the column and is further preheated in the coke heater and flows into the coke drum. When the coke drum is filled, the heated streams from the coke heater are sent to the other drum.

The reaction involved in the delayed coking is partial vaporization and partial cracking. It can process VR, visbreaker residue, and FCC residual, and produces gases, naphtha, fuel oil, gas oil, and coke. The product distribution depends mainly on the CCR value of the
Some empirical relationships are available to predict the yield of various products as expressed in the following equations (Kumar 2009):

\[
\text{Coke yield (wt.\%)} = 1.6 \times (\text{wt.\% feed CCR})
\]

\[
\text{Gas (C}_4\text{)(wt.\%)} = 7.8 + 0.144 \times (\text{wt.\% feed CCR})
\]

\[
\text{Gasoline (wt.\%)} = 11.29 + 0.343 \times (\text{wt.\% feed CCR})
\]

\[
\text{Gas oil (wt.\%)} = 100 - \text{wt.\% coke} - \text{wt.\% gas} - \text{wt.\% gasoline}
\]

Other feedstock properties that influence the product distribution are characterization factor, sulfur content, and metal content. The characterization factor is defined as ([Mean average boiling point in °R]^{1/3}/Specific gravity 60°F/60°F). Lower characterization factor gives higher coke yield (McKetta 1992). Operating parameters such as temperature, pressure, and recycle ratio also influence the product distribution as well as the quality of coke. Higher temperature increases the gas yield and reduces the coke yield. However, hardness of the coke increases with an increase in temperature. Higher pressure and recycle ratio increase gas as well as coke formation. Lower recycle ratio is desirable for more liquid products.

In the delayed coking process, three types of reactions such as dehydrogenation, rearrangement, and polymerization are involved simultaneously. Through the dehydrogenation step, an aromatic hydrocarbon produces one hydrogen radical and one aromatic free radical. The rearrangement step produces more stable aromatic ring system as a building block for graphite. The polymerization step of aromatic ring systems in the liquid phase produces coke.
In this process, coke yield increases with an increase in the coke drum pressure (keeping the reactor outlet temperature same). This is attributed to the fact that more condensation and polymerization reactions take place at higher pressure. Further, with an increase in the reactor outlet temperature as well as the coke drum temperature, coke yield decreases, which indicates that more cracking takes place at higher temperature. Different types of cokes such as sponge coke, needle coke, and shot coke are formed depending upon the feedstock quality as well as the operating parameters, which are discussed as follows:

**Sponge coke:** It is porous and has a sponge-like appearance. It is formed when the asphaltene content in the VR is low to moderate. It is basically used as a fuel; few cokes with low metal and sulfur content (<2%) can be used as the anode material.

**Needle coke:** It is a high-value product and is obtained through the delayed coking process. Currently, in India, the delayed coking units are producing only sponge/fuel coke, and all the indigenous requirements of needle coke are being met through imports. Premium-grade needle coke production technology is a closely guarded secret and not easily available from licensors. Needle coke, which is an essential precursor for the ultrahigh-power graphite electrodes in electric arc furnaces, is produced by delayed coking. Characteristics such as low coefficient of thermal expansion (CTE), high density, high electrical conductivity, and low puffing are essentially required for a quality needle coke. Such qualifying characteristics have been recognized to be strongly influenced by the nature of feedstock and operating/carbonization conditions. Operating parameters also play an important role in establishing the crystalline structure of needle coke. It has a needlelike appearance and can be produced from the feedstock containing more aromatics. Decant oil from the FCC unit after hydrodesulfurization can be a suitable feedstock for needle coke. It can be used as a high-quality electrode due to its very low electrical resistance and CTE.

**Shot coke:** High asphaltene containing feedstocks at high coke drum temperature produce shot coke. It is not a desirable product and is used as a fuel with sponge coke.

### 3.2.3 Fluid Catalytic Cracking

It is an important conversion process when more gasoline production is required from heavier petroleum fraction such as VGO, deasphalted oil (DAO), and coker gas oil. It can produce higher quality liquid and gaseous products than thermal cracking. In this process, the feedstocks crack with the help of a fluidized catalyst powder in the reactor. The used (spent) catalyst is activated for reuse in the regenerator. The products are fractionated into different parts. Two types of design such as side by side and stack type are available in the FCC unit. In the first type, the reactor and the catalyst regenerator are two separate vessels, whereas in the second type, these are continued in a single vessel. The reactor and regenerator are considered to be the heart of the FCC unit.

Figure 3.7 shows the process flowsheet of a side-by-side configuration FCC unit. This unit operates in a closed circuit, and pressure balance plays an important role in the operation of this unit. Normally, the preheated feedstock injected into the catalyst riser (~540°C) is vaporized and cracked into smaller molecules by the catalytic action of hot catalyst powder in the riser within 2–4 s. The hydrocarbon vapors help to fluidize the catalyst powder, which is also mixed with the hydrocarbon vapors and enters the reactor at approximately 535°C and ~1.72 bar pressure. The reactor contains a two-stage cyclone that
helps to separate the catalyst powder from the products and directs the deactivated (spent) catalysts to the regenerator through the steam stripper to remove hydrocarbon molecules attached with the catalysts. Deactivation of catalyst takes place due to coke deposition, and in the regenerator, the spent catalyst gets free from the deposited coke by oxidation at high temperature (715°C) and pressure (2.14 bar). The heat generated by exothermic combustion in the regenerator is partially carried over by the regenerated catalysts, which enter into the riser and mix with the feedstock as well as provide heat for endothermic cracking reaction. The hot vapor coming out from the reactor is further fractionated into different product streams. Use of riser internals and modification of the feed injection system have improved the performance of the FCC process. The riser internals promote ideal plug flow conditions in the riser by reducing the density and velocity variation inside the riser. Improvement in the riser termination technology, with the help of the two-stage cyclone system, results in controlled cracking and desired product yield. Development of new nozzles for injecting the FCC feedstock into the riser has been able to maintain proper mixing of it with catalyst and as a consequence the temperature profile in riser (Chen 2004).

The FCC process has been modified to produce gasoline- as well as olefin-rich products from heavy residues. The Universal Oil Products (UOP)’s Resid FCC (RFCC) process produces gasoline and lighter components from the VR using a two-stage stacked regenerator with their proprietary catalysts. The I-FCCSM process, which combines Lummus Technology’s FCC process with the proprietary INDMAX catalyst of Indian Oil Corporation Limited, Tamil Nadu, India, can selectively produce propylene and other light olefins. It also provides feedstock conversion (up to 45%). The operating conditions for this process are as follows: riser reactor 530°C–600°C and catalyst-to-oil ratio 12–20. The partial pressure of hydrocarbon is also lower than that of the conventional FCC process (Soni 2009).

### 3.2.4 Solvent Deasphalting Process

When asphaltene and metal content are high in the heavy residue, the solvent deasphalting (SDA) process becomes attractive for its upgradation, as these materials adversely
affect the performance of catalysts for hydrodesulfurization, HDC, or any catalytic conversion of the heavy residues. In the SDA process, asphaltenes from the heavy residue are removed through liquid–liquid extraction procedure, in which a paraffinic solvent (C₃–C₇) is used as an extracting solvent. The paraffinic components in the heavy residue are separated from the asphaltenes and come out as extracts with the solvent and form DAO. The asphaltenes settle down in the extractor. In VR, about 80% asphaltene is present, which can be converted into diesel after separation of asphaltenes and processing of DAO. Figure 3.8 shows a typical process flowsheet for an SDA plant. From this figure, it is evident that both asphaltenes and DAO pass through the solvent recovery step; the recovered solvent is recycled and reused to mix the heavy residue. To recover the solvent from DAO, it is heated and flashed, whereas the solvent entrained in asphaltenes is removed by heating it above the minimum asphalt pumping temperature to ensure the flow ability of asphaltenes after solvent recovery. Solvent recovery above the critical conditions of the solvent can improve the energy efficiency and reduce utility consumption and capital investment by introducing a compact unit. The asphaltene is a feedstock for road making and gasification, whereas the DAO after solvent recovery is hydrotreated to remove sulfur and acids as well as to increase the yield in downstream cracking. DAO produced through propane deasphalting can also be used to produce lube base stock.

The quantity and quality of DAO depends on the solvent used, solvent-to-feed ratio, pressure, temperature, extractor type, and so on. Higher molecular weight solvent allows heavier and resinous molecules to enter into DAO, which results in higher DAO yield but reduces its quality as these heavier molecules contain impurities. Thus, to achieve a proper DAO quality, solvent selection is important. Increasing the solvent-to-feed ratio, the asphaltene precipitation can be increased up to 10 times; however, a further increase in
this ratio does not affect asphaltene settling much (Gonzalez et al. 2004). An increase in the extractor temperature reduces the density of the solvent; as a result, DAO yield reduces. An increase in the pressure increases the density of the solvent; consequently, DAO yield increases. In refinery, a well-balanced approach is applied to select these parameters for optimum DAO production, and normally variation of pressure is not well accounted due to mechanical and process restrictions (Sattarin et al. 2006). Typical operating conditions for the SDA process using propane, butane, and pentane are provided in Table 3.4.

Kellogg Brown and Root (KBR), UOP, and Foster Wheeler are the major technology licensors for SDA. The French Institute of Petroleum, France; the Research Institute of Petroleum Processing, China; and Engineers India Limited with the Indian Institute of Petroleum, Dehradun, India have also transferred this technology to some industries. Deasphalting tower may contain baffle trays/louvre trays, rotating disc contractor, packing (random/structured), or parallel interceptor plate assemblies. The residuum oil supercritical extraction (ROSE) unit contains a proprietary tray-type Lubemax internal and produces a superior quality DAO suitable for the production of lube base stock.

To improve the economy of the SDA process, a gasification unit can be integrated with the SDA unit. In such case, value addition takes place through the production of syngas from asphaltenes in the gasifier unit. The produced syngas can be used as the source of sensible heat as well as many chemicals (Ogawa 1996).

### 3.2.5 HDC Technology

In this process, cracking of heavy petroleum fractions, including residues, takes place in the presence of hydrogen and a catalyst (Rogers and Stormont 1968), and produces lesser coke than thermal cracking. Different types of reactors such as fixed bed, moving bed, ebullated bed, and slurry-phase reactors are used (Cherzer and Gruia 1996). In the fixed bed reactor, normally multiple beds of catalysts are present, whereas in the moving bed reactor, expansion of the catalyst bed takes place, which gives lesser pressure drop (Ancheyta and Speight 2007). High API feedstocks, including the middle distillate, are hydrotreated in the fixed bed reactor, whereas for complex feedstocks, the moving bed or ebullated bed reactors are the preferred option. A combination of both fixed bed and moving bed/ebullated bed reactors in series may be used if the feedstock quality is very low (Ramirez et al. 2007). Although a mechanism is similar for all the reactor types, tolerance of impurities differs among them. Experimental conditions and catalyst properties also influence the product selectivity in these reactors. Nanostructured catalysts have been developed for the HDC of heavy residues (API gravity 2.3°) in recent years, which may improve the efficiency of

<table>
<thead>
<tr>
<th>Conditions Solvents Used in SDA Process</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Solvent Ratio (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>50–80</td>
<td>35–40</td>
<td>6–9</td>
</tr>
<tr>
<td>Butane</td>
<td>100–130</td>
<td>40</td>
<td>4–7</td>
</tr>
<tr>
<td>Pentane</td>
<td>170–210</td>
<td>40</td>
<td>3–5</td>
</tr>
</tbody>
</table>

the process (Hur et al. 2014). Comparison of different technologies for the upgradation of heavy petroleum fractions is provided in Figure 3.9.

From this figure, it is evident that the delayed coking is a process with low capital cost and relatively high conversion. It produces petcoke that can further be used through different routes. However, the economic feasibility of this process may be tightened in future due to increased cost associated with strict environmental norms.

### 3.2.6 Gasification

The low-cost (sometimes negative cost due to environmental regulation) carbon-rich products such as petcoke and asphaltenes, generated through carbon rejection routes of residue upgradation, can be utilized through gasification to convert them into syngas, which can further be upgraded to various valuable products such as liquid fuel, hydrogen, and chemicals. Other heavy petroleum fractions can also be utilized through this route. In gasification, the carbonaceous feedstocks are heated in a controlled amount of oxygen/air to produce the syngas. A controlled amount of steam is also added to feedstocks such as petcoke where the moisture content of the feedstock is less. The major reactions involved in the gasifier are presented as follows:

\[
\begin{align*}
C + \frac{1}{2}O_2 \rightarrow CO & \quad \Delta H_{298}^{0} = -110.5 \text{ kJ/mol} \quad (3.15) \\
C + O_2 \rightarrow CO_2 & \quad \Delta H_{298}^{0} = -393 \text{ kJ/mol} \quad (3.16) \\
C + CO_2 \rightarrow 2CO & \quad \Delta H_{298}^{0} = 172 \text{ kJ/mol} \quad (3.17) \\
C + H_2O \rightarrow CO + H_2 & \quad \Delta H_{298}^{0} = 131.4 \text{ kJ/mol} \quad (3.18)
\end{align*}
\]
The important minor reactions involved in the gasification are expressed as follows (Mondal et al. 2011):

\[
\text{CO} + 3\text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^0_{298} = -205 \text{ kJ/mol} \quad (3.19)
\]

\[
\text{CO} + \text{H}_2 \longrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^0_{298} = -40.9 \text{ kJ/mol} \quad (3.20)
\]

\[
\text{C} + 2\text{H}_2 \longrightarrow \text{CH}_4 \quad \Delta H^0_{298} = -74.8 \text{ kJ/mol} \quad (3.21)
\]

The gasification with \( \text{CO}_2 \) is also called as the Boudouard reaction, and Equation 3.17 is called as the water shift reaction. In the above equations, only carbon has been considered. However, in carbonaceous feedstocks, many other elements are also available in terms of many complex compounds. Thus, efforts are made to generalize the reactions involved in gasification. It is assumed that when the feedstock comes in contact with high heat in the gasifier, it produces volatilized hydrocarbons and char (Smoot and Smith 1985). The hydrocarbon vapor reacts with oxygen to give syngas as follows (Shoko et al. 2006):

\[
\text{C}_n\text{H}_m + \frac{1}{2} n\text{O}_2 \longrightarrow \frac{1}{2} m\text{H}_2 + n\text{CO} \quad (3.22)
\]

However, the gasification of char takes place as per the overall reaction (Smoot and Smith 1985):

\[
\text{CH}_x\text{O}_y\text{Z}(\text{char}) + (1 - y)\text{H}_2\text{O} \longrightarrow (x/2 + 1 - y)\text{H}_2 + \text{CO} \quad (3.23)
\]

A further generalization approach represents gasification reactions through Equations 3.24 through 3.27. It is assumed that char is composed of C, H, O, N, S, and metals.

\[
\text{CH}_x\text{O}_{o+x}N_n\text{S}_sZ + a\text{O}_2 \longrightarrow b\text{CO}_2 + c\text{CO}_2 + d\text{H}_2\text{O} + e\text{H}_2\text{S} + f\text{N}_2 + \text{ZO}_x \quad (3.24)
\]

\[
\text{CH}_x\text{O}_{o+x}N_n\text{S}_sZ + \text{CO}_2 \longrightarrow 2\text{CO} + \frac{o}{2}\text{H}_2\text{O} + \left(\frac{h}{2} - s - o\right)\text{H}_2 + s\text{H}_2\text{S} + \frac{n}{2}\text{N}_2 + \text{ZO}_x \quad (3.25)
\]

\[
\text{CH}_x\text{O}_{o+x}N_n\text{S}_sZ + (1 - o)\text{H}_2\text{O} \longrightarrow \text{CO} + \left(1 - o + \frac{h}{2} - s\right)\text{H}_2 + s\text{H}_2\text{S} + \frac{n}{2}\text{N}_2 + \text{ZO}_x \quad (3.26)
\]

\[
\text{CH}_x\text{O}_{o+x}N_n\text{S}_sZ + (2 + o + s - \frac{h}{2})\text{H}_2 \longrightarrow \text{CH}_4 + o\text{H}_2\text{O} + s\text{H}_2\text{S} + \frac{n}{2}\text{N}_2 + \text{ZO}_x \quad (3.27)
\]

The following equation is also considered to justify the presence of COS in syngas:

\[
\text{H}_2\text{S} + \text{CO}_2 \longrightarrow \text{COS} + \text{H}_2\text{O} \quad (3.28)
\]

The properties of syngas produced through the gasification of a carbonaceous feedstock depend on the operating conditions and the type of gasifier used. A typical composition of syngas produced from petcoke and petroleum residues is as follows: 25%–30% \( \text{H}_2 \) (v/v), 30%–60% \( \text{CO} \) (v/v), 5%–15% \( \text{CO}_2 \) (v/v), and 2%–3% \( \text{H}_2\text{O} \) (v/v) (Gupta 2005; Gills 2006). A small amount of \( \text{CH}_4, \text{H}_2\text{S}, \text{N}_2, \text{NH}_3, \text{HCN}, \text{Ar}, \text{COS}, \text{Ni}, \) and Fe carbonyls may also be present (Gills 2006).
Different types of gasifiers such as fixed bed, fluidized bed, entrained bed, and transport reactor are available, which are operated under different conditions with different particle sizes of feedstocks and show different efficiencies as well as product qualities. The salient features of these gasifiers are summarized in Table 3.5.

Among these gasifiers, the fixed bed gasifier is suitable for handling highly active feedstocks such as coal and biomass. In this gasifier, the feedstock enters from the top and the gasifying medium is sent from the bottom; hence, the feedstock comes in contact with hot gas with increasing temperature when the feedstock proceeds through different zones.
Downstream Processing of Heavier Petroleum Fractions

(from the drying zone to the combustion zone) of the gasifier as shown in Figure 3.10. Although a maximum temperature (~1800°C) is available in the combustion zone of this gasifier, the temperature along the height of the gasifier decreases with an increase in height, and at the exit of gas, the temperature reduces to 600°C. For this reason, the product gas contains more tar and phenolic compounds.

In case of the fluidized bed gasifier, both the feedstock and the gasifying medium are injected at the bottom of the gasifier (Warnecke 2000). A uniform temperature along the length of the gasifier is maintained due to high level of back-mixing. The temperature in the gasifier remains below the ash fusion temperature (900°C–1050°C); as a result, no ash melting and clinker formation take place. It is a more suitable gasifier type for coal gasification.

In case of the entrained bed reactor, the feedstock and gasifying medium enter into the gasifier from the top, and a high temperature (1500°C) is maintained in the gasifier throughout its length; thus, it produces good-quality syngas with negligible tar and phenolic. This type of gasifier is more suitable to gasify less reactive feedstocks such as pet coke and heavy petroleum fractions. Entrained bed gasifier produces slag due to very high temperature inside it, which shows an adverse impact on the burner and refractory life. To reduce the ash melting temperature of feedstocks, fluxes such as limestone can be added, which can also fix some amount of sulfur present in the feedstocks. Entrained bed gasifiers may handle feedstocks in the dry phase or slurry phase. Shell and Prenflo gasifiers are the best-known dry feeding gasifiers, whereas Texaco and Destec gasifiers are the best-known slurry feeding entrained bed gasifiers. The salient features of these gasifiers are summarized in Table 3.6.

Syngas produced from the gasification of the heavy petroleum fractions can be used in various downstream processing. In recent years, to make the process more economic, the concepts of integrated gasification combined cycle (IGCC) and polygeneration have been utilized. Integration of heat application with other syngas utilization routes such

FIGURE 3.10
as hydrogen production, Fischer–Tropsch synthesis, and chemical synthesis makes the process more economic. However, the requirements of purity of syngas for various downstream processing are different, and to meet these specie qualities, the conditioning and cleaning of syngas is essential. Conditioning is used to improve the \( \text{H}_2 : \text{CO} \) ratio in syngas, which is carried out through water–gas shift reaction, whereas cleaning involves the separation of particulates and acid gases such as \( \text{H}_2\text{S} \), \( \text{COS} \), and \( \text{CO}_2 \). The shift reactions can be performed either before cleaning acid gases (sour shift) or after removing acid gases (sweet gas shift). A comparison of these two types of shift reactions is provided in Table 3.7.

For the removal of acid gases from the syngas, both wet and dry processes are used. The wet process is based on physical, chemical, and both physical and chemical absorption, whereas the dry process involves the adsorption of acid gas components in warm adsorbent bed. Some important wet processes for the removal of acid gases are Rectisol, Selexol, Sulfinol, and so on; metal oxides such as ZnO are used as an adsorbent in the dry process. The spent adsorbent is regenerated at high temperature. Among these processes, Rectisol is having the maximum removal capacity; however, it is the costliest process. Some important gasifier units running on the heavy petroleum fraction along with downstream application of syngas are summarized in Table 3.8.

### Table 3.6
Comparison of Various Gasifiers

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Texaco</th>
<th>Shell</th>
<th>Destec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed system</td>
<td>Slurry</td>
<td>Dry</td>
<td>Slurry (horizontal and vertical)</td>
</tr>
<tr>
<td>Gasifier configuration</td>
<td>Single-stage downflow</td>
<td>Single-stage upflow</td>
<td>Two stage</td>
</tr>
<tr>
<td>Gasifier wall</td>
<td>Refractory</td>
<td>Membrane</td>
<td>Refractory</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>41</td>
<td>30</td>
<td>27.6</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1250–1550</td>
<td>2000</td>
<td>1371–1537</td>
</tr>
<tr>
<td>Coal size</td>
<td>&lt;0.1 mm</td>
<td>&lt;0.1 mm</td>
<td>&lt;100 μm</td>
</tr>
</tbody>
</table>


### Table 3.7
Comparison of Sweet and Sour Shift Reactions

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Sweet Shift</th>
<th>Sour Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical flowsheet</td>
<td>Two High temperature shift (HTS) and one Low temperature shift (LTS) conversion stages with cooling between the reactors</td>
<td>Two to three conversion stages with heat exchangers and sometimes steam addition as required</td>
</tr>
<tr>
<td>CO conversion</td>
<td>Within two HTS steps, sweet gas shift can reduce CO conversion from 44.6% to 2.1%. The residual CO can be further converted into 0.5% in the LTS step</td>
<td>From 44.6% to 1.8% within two steps using a slightly higher amount of steam. To reach a CO level below 1%, large quantity of steam is added in the third reactor before shift reaction</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Usually more expensive</td>
<td>Usually less expensive</td>
</tr>
<tr>
<td>Reactor</td>
<td>The size of catalyst bed is smaller</td>
<td>The size of catalyst bed is higher</td>
</tr>
</tbody>
</table>

### TABLE 3.8
Major Electricity-Producing Gasification Plants around the World

<table>
<thead>
<tr>
<th>Country (1)</th>
<th>Plant Name (2)</th>
<th>Technology (3)</th>
<th>Feedstock (4)</th>
<th>Products (5)</th>
<th>Syngas Cleaning Option</th>
<th>Year (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>Dalan Chemical Industrial Corp.</td>
<td>Texaco</td>
<td>Visbreaker residue</td>
<td>Ammonia</td>
<td>Rectisol</td>
<td>1995</td>
</tr>
<tr>
<td>China</td>
<td>Inner Mongolia Fertilizer Co.</td>
<td>Shell</td>
<td>VR</td>
<td>Ammonia</td>
<td>Rectisol</td>
<td>1996</td>
</tr>
<tr>
<td>China</td>
<td>Juijang Petrochemical Co.</td>
<td>Shell</td>
<td>VR</td>
<td>Ammonia</td>
<td>Rectisol</td>
<td>1996</td>
</tr>
<tr>
<td>China</td>
<td>Lanzhou Chemical Industrial Co.</td>
<td>Shell</td>
<td>VR</td>
<td>Ammonia</td>
<td>Rectisol</td>
<td>1998</td>
</tr>
<tr>
<td>China</td>
<td>Fujian project</td>
<td>Shell</td>
<td>Deasphalted rock</td>
<td>Electricity and H₂</td>
<td>Rectisol</td>
<td>2006</td>
</tr>
<tr>
<td>Europe</td>
<td>Unspecified plant</td>
<td>Shell</td>
<td>Residue</td>
<td>Electricity</td>
<td></td>
<td>2005</td>
</tr>
<tr>
<td>France</td>
<td>Normandie IGCC plant</td>
<td>Texaco</td>
<td>Fuel oil</td>
<td>Electricity, steam, and H₂</td>
<td>Selexol</td>
<td>2005</td>
</tr>
<tr>
<td>France</td>
<td>–</td>
<td>Texaco</td>
<td>Refinery residue</td>
<td>H₂</td>
<td>Selexol</td>
<td>2006</td>
</tr>
<tr>
<td>Germany</td>
<td>Hydro AgriBrunsbittel</td>
<td>Shell</td>
<td>Heavy VR</td>
<td>Ammonia</td>
<td>Rectisol</td>
<td>1978</td>
</tr>
<tr>
<td>Germany</td>
<td>Leuna methanol Anlage</td>
<td>Shell</td>
<td>Visbreaker residue</td>
<td>H₂, methanol, and electricity</td>
<td>Rectisol</td>
<td>1985</td>
</tr>
<tr>
<td>Germany</td>
<td>SARGmbH</td>
<td>Texaco</td>
<td>VR</td>
<td>H₂ and chemicals</td>
<td>Sulfinol</td>
<td>1988</td>
</tr>
<tr>
<td>Germany</td>
<td>Slurry/oil gasification</td>
<td>Lurgi MPG</td>
<td>Oil and slurry</td>
<td>Electricity and methanol</td>
<td>MDEA</td>
<td>1968</td>
</tr>
<tr>
<td>Holland</td>
<td>Pernis refinery</td>
<td>Shell</td>
<td>Resid oil</td>
<td>Electricity</td>
<td></td>
<td>1997</td>
</tr>
<tr>
<td>India</td>
<td>Gujrat National Fertilizer Co.</td>
<td>Texaco</td>
<td>Refinery residue</td>
<td>Ammonia</td>
<td>Rectisol</td>
<td>1982</td>
</tr>
<tr>
<td>India</td>
<td>Bhatinda IGCC</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Electricity</td>
<td></td>
<td>2005</td>
</tr>
<tr>
<td>Italy</td>
<td>ISAB Energy Project</td>
<td>Texaco</td>
<td>ROSE asphalt/heavy oil</td>
<td>Electricity, H₂ and steam</td>
<td>MDEA</td>
<td>2000</td>
</tr>
<tr>
<td>Italy</td>
<td>SARLUX GCC/H₂ plant</td>
<td>Texaco</td>
<td>Visbreaker residue</td>
<td>Electricity, H₂ and steam</td>
<td>Selexol</td>
<td>2001</td>
</tr>
<tr>
<td>Italy</td>
<td>ApiEnergis S.p.A</td>
<td>Texaco</td>
<td>Visbreaker residue</td>
<td>Electricity, H₂ and steam</td>
<td>Selexol</td>
<td>2001</td>
</tr>
<tr>
<td>Italy</td>
<td>Agip IGCC</td>
<td>Shell</td>
<td>Visbreaker residue</td>
<td>Electricity and H₂</td>
<td>Amine</td>
<td>2003</td>
</tr>
<tr>
<td>Italy</td>
<td>Sannazzaro GCC plant</td>
<td>Texaco</td>
<td>Visbreaker residue</td>
<td>Electricity</td>
<td></td>
<td>2005</td>
</tr>
<tr>
<td>Japan</td>
<td>Marufu IGCC plant</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Electricity</td>
<td></td>
<td>2004</td>
</tr>
<tr>
<td>Japan</td>
<td>Nippon Pet. Ref. CO.</td>
<td>Texaco</td>
<td>VR</td>
<td>Electricity</td>
<td>ADIP</td>
<td>2004</td>
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<tr>
<td>Japan</td>
<td>Yokohama Cogen/B</td>
<td>Texaco</td>
<td>VR</td>
<td>Electricity</td>
<td></td>
<td>2003</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Pernis Shell gasifier, Hydrogen plant</td>
<td>Shell</td>
<td>Visbreaker residue</td>
<td>H₂ and Electricity</td>
<td>Rectisol</td>
<td>1997</td>
</tr>
</tbody>
</table>

(Continued)
TABLE 3.8 (Continued)
Major Electricity-Producing Gasification Plants around the World

<table>
<thead>
<tr>
<th>Country (1)</th>
<th>Plant Name (2)</th>
<th>Technology (3)</th>
<th>Feedstock (4)</th>
<th>Products (5)</th>
<th>Syngas Cleaning Option</th>
<th>Year (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poland</td>
<td>Gdansk IGCC plant</td>
<td>Texaco</td>
<td>Visbreaker residue</td>
<td>Electricity, H₂, and steam</td>
<td>Rectisol</td>
<td>2005</td>
</tr>
<tr>
<td>Portugal</td>
<td>QuimigalAducos</td>
<td>Shell</td>
<td>VR</td>
<td>Ammonia</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>Singapore</td>
<td>Chawan IGCC plant</td>
<td>Texaco</td>
<td>Residual oil</td>
<td>Electricity, H₂, and steam</td>
<td>Flexorb</td>
<td>2000</td>
</tr>
<tr>
<td>Singapore</td>
<td>Singapore Syngas</td>
<td>Texaco</td>
<td>Visbreaker tar</td>
<td>H₂ and CO (for acetic acid)</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>Puertollano GCC plant</td>
<td>PRENFO</td>
<td>Coal and petcoke</td>
<td>Electricity</td>
<td>MDEA</td>
<td>1997</td>
</tr>
<tr>
<td>Spain</td>
<td>Bilbao IGCC plant</td>
<td>Texaco</td>
<td>VR</td>
<td>Electricity and H₂</td>
<td>2005</td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>PIEMSA</td>
<td>Texaco</td>
<td>Visbreaker tar</td>
<td>Electricity and H₂</td>
<td>MDEA</td>
<td>2006+</td>
</tr>
<tr>
<td>USA</td>
<td>Wabash River Energy Ltd.</td>
<td>E-GAS (Destec/Dow)</td>
<td>Petcoke</td>
<td>Electricity</td>
<td>MDEA</td>
<td>1995</td>
</tr>
<tr>
<td>USA</td>
<td>Delaware clean energy Cogen. project</td>
<td>Texaco</td>
<td>Fluid petcoke</td>
<td>Electricity and steam</td>
<td>MDEA</td>
<td>2001</td>
</tr>
<tr>
<td>USA</td>
<td>Coffeyville Refinery</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>H₂ and NH₃</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>Farmland Industries Lnc.</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Ammonia</td>
<td>Selexol</td>
<td>2000</td>
</tr>
<tr>
<td>USA</td>
<td>ExxonMobil Baytown Syngas project</td>
<td>Texaco</td>
<td>Deasphalter bottom</td>
<td>H₂ and CO</td>
<td>Rectisol</td>
<td>2001</td>
</tr>
<tr>
<td>USA</td>
<td>Valero Refinery</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Electricity, steam</td>
<td>2002</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>Port Arthur GCC Project</td>
<td>E-GAS</td>
<td>Petcoke</td>
<td>Electricity</td>
<td>2005</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>Lake Charles IGCC plant</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Electricity, H₂, and steam</td>
<td>2005</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>Deer Park GCC plant</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Electricity, syngas, and steam</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>Polk Country gasification plant</td>
<td>Texaco</td>
<td>Petcoke</td>
<td>Electricity</td>
<td>2005</td>
<td></td>
</tr>
</tbody>
</table>

3.2.7 Biological Processing of Heavy Fractions

Biotechnological processes are being explored around the world to develop new routes for energy production due to their low cost and eco-friendly nature. Recently, it has been reported that some microbial strains can degrade various polynuclear aromatic hydrocarbons (PAHs) such as anthracite, mono-aromatic hydrocarbons such as toluene, or aliphatic hydrocarbons such as n-alkanes from petroleum-contaminated sites (Whyte et al. 1997; Kim et al. 2001; Östberg et al. 2007; Liu et al. 2010; Karimi et al. 2013).

*Bacillus cereus* has been used for the remediation of petroleum-polluted soils (Gupta and Gera 2015). Several integral parameters including the conditions for microbial degradation activity (e.g., presence of nutrients, oxygen, pH, and temperature); the quality, quantity, and bioavailability of the contaminants (e.g., particle size distribution); and the soil characteristics have been found to affect the rate of microbial degradation of hydrocarbons in soils (Gupta and Gera 2015). Therefore, the bacteria with high physicochemical endurance and degradation ability could be a proper choice not only in bioremediation but also in degradation of PAHs to smaller molecules. These PAHs are present in many heavy petroleum fractions. Thus, further development in this area may produce new biological routes for the upgradation of heavy residues in future. However, an extensive research and development is required in this field.

3.3 Concluding Remarks

The quality of petroleum crude is degrading day by day, which is producing heavier petroleum fractions and forcing the refiners to process the heavier fractions for value addition to the process. Different types of upgradation processes based on hydrogen addition and carbon rejection are used to utilize the heavier fraction. Various conventional methods such as visbreaking, delayed cracking, FCC, and HDC have their own advantages and disadvantages. The conventional FCC process uses VGO, DAO, and so on effectively; however, for handling the residue, the RFCC process can be used. Similarly, methods such as I-FCCSM have been developed to get more olefin-rich products from the heavy residue. Gasification followed by polygeneration with the IGCC concept can improve the economics of heavy residue utilization. Efforts are also made to develop new biotechnology and nanotechnology for the utilization of heavy petroleum fractions.

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