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PROPERTIES OF HEAVY OILS

1.1 INTRODUCTION

The physical properties and chemical composition of petroleum vary from one source to another. The petroleum fractions, that is, distillates, are separated from each other by fractionated distillation according to boiling points. The lighter fractions, straight-run naphtha and gas oil, are used to produce commercial fuels, gasoline and diesel, respectively. However, bottoms-of-barrel (heavy residua) obtained by distillation of crude oils need further processing. An example of chemical composition of crude oils is given in Table 1.1 in terms of SARA (Saturates, Aromatics, Resins, and Asphaltenes) analysis. It is clearly seen that the composition varies remarkably, for instance, asphaltenes content in crude oils ranges from 5.9 to 23.9 wt%, concentrating more in the heavy petroleum. Another important observation is that heteroatoms (N and S) and metals concentrate in asphaltene fraction. In other words, most of these crude oil impurities are of asphaltenic nature. These aspects and the complex nature of asphaltenes are crucial facts when studying catalyst deactivation.

In the particular case of heavy crude oil, the typical and widely accepted definition is that heavy petroleum is any type of crude oil that does not flow easily. API gravity is the most common parameter to define how heavy or light a crude oil is. API gravity is correlated with the specific gravity (sg) or density by means of the following equations:

$$\text{API gravity} = \frac{141.5}{\text{sg}^{60°\text{F}}_{60°\text{F}}} - 131.5 \tag{1.1}$$

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TABLE 1.1 Example of Chemical Composition of Various Crude Oils

	wt%	Crude Oil (wt% of the total)				AR (345 °C+)	
		S	N	V	Ni	Ni	V
				Maya (21°API)			
Saturates	21.2	0.9	3.3	–	–	–	–
Aromatics	27.1	24.4	8.2	0.4	3.3	2.7	2.7
Resins	30.6	38.7	39.6	17.9	17.7	13.0	12.9
Asphaltenes	21.1	36.0	48.9	81.7	79.0	84.3	84.4
				Kern River (13°API)			
Saturates	23.3	0.2	2.7	–	–	–	–
Aromatics	30.7	30.7	4.2	7.5	4.5	1.8	2.7
Resins	40.1	60.3	77.3	52.7	63.0	22.8	16.7
Asphaltenes	5.9	8.8	15.8	39.8	32.5	75.4	80.6
				Arabian Heavy (27°API)			
Saturates	0.2	6.7	–	–	–	–	0.2
Aromatics	29.6	8.4	3.4	10.4	5.2	1.6	29.6
Resins	46.3	43.8	25.2	28.0	14.2	11.8	46.3
Asphaltenes	23.9	41.1	71.4	61.6	80.6	86.6	23.9

AR, Atmospheric residue.

$$\mathrm{sg}_{60^\circ\mathrm{F}}^{60^\circ\mathrm{F}} = \frac{141.5}{\text{API gravity} + 131.5} \tag{1.2}$$

Heavy crude oils possess low API gravity; thus, the API gravity is an inverse measure of the density of petroleum. Heavy crude oils are generally considered as those samples having an API gravity of less than 20°, while extra-heavy crude oils have less than 10°API, both with gas-free viscosity between 100 and 10,000 cP at original reservoir temperature. Heavy oils are then characterized by high viscosities (i.e., resistance to flow) and high densities compared with light crude oil.

In general, heavy oils exhibit a wide range of physical properties. While properties such as viscosity, density, and boiling point may vary widely, the ultimate or elemental analysis varies over a narrow range for a large number of samples. The carbon content is relatively constant, while the hydrogen and heteroatom contents are responsible for the major differences in various heavy oils.

Heavy oils are constituted by heavy hydrocarbons and several metals, predominantly in the form of porphyrins. Heavy feeds also contain aggregates of resins and asphaltenes dissolved in the oil fraction held together by weak physical interactions.

The main problems that heavy crude oil presents during different steps of storage, transportation, and processing are low processing capacity in the refineries, low mobility through the reservoir because of its high viscosity, and difficult and costly transportation from the platform to the ground and to the refineries.

For transportation purposes, viscosity and density (or API gravity) are the most important parameters. Frequently, heavy crude oils with an API gravity of less than 16° cannot be transported without a prior reduction in their viscosity, as this type of crudes come along with viscosities ranging from a few thousands to millions of centipoises (cP) at reservoir temperature, while 250 cSt at 100 °F is a normal maximum desired pipeline viscosity.

Due to the different properties that the various crude oils exhibit around the world, several classifications have been proposed. The classifications of petroleum take into consideration physical properties, distillates properties, chemical structure, origin, and so on. For instance, if the sulfur content in a crude oil is high, the petroleum is classified as "sour," while if this content is low the petroleum is termed as "sweet." On the other hand, if the API gravity is low, the petroleum is termed as "heavy" and if the API gravity is high the petroleum classification is termed "light." Generally speaking, petroleum is classified as follows (Ancheyta and Speight, 2007):

- *Light Crude Oil*. It is also called conventional oil and has an API gravity of at least 20° and a viscosity less than 100 cP.
- *Heavy Crude Oil*. It is a dense and viscous oil that is chemically characterized by its high content of asphaltenes (very complex and large molecules). Its upper limit of API gravity is 20° and a viscosity of 100 cP.
- *Extra-Heavy Crude Oil*. It has an API gravity of less than 10°.
- *Bitumen*. It is also called "tar sands" or "oil sands." It has similar properties to that of heavy oil but is yet more dense and viscous. The main difference between bitumen and heavy oil is that the former does not flow at all. Natural bitumen is oil having a viscosity of greater than 10,000 cP.

Heavy crude oils have low API gravity and high amount of impurities. In general, it is known that the lower the API gravity, the higher the impurities content. Such properties make the processing of heavy feeds different from that used for light distillates, causing several problems such as permanent catalyst deactivation in catalytic cracking and hydrocracking processes caused by metal deposition, temporary deactivation of acid catalysts due to the presence of basic nitrogen, higher coke formation, and lower liquid product yield as a result of high Conradson carbon and asphaltene contents, products with high content of sulfur.

The complex nature of heavy crude oils is the reason why their refining becomes so difficult. Therefore, an evaluation of the overall chemical and physical properties of petroleum feeds is mandatory to determine the processing strategy. Apart from having low API gravity (high density), high viscosity, and high initial boiling point, heavy oils exhibit higher content of sulfur, nitrogen, metals (Ni and V), and high-molecular-weight material (asphaltenes).

1.2 REFINING OF PETROLEUM

A petroleum refinery is mainly designed to produce fuels, for example, gasoline, jet fuel, and diesel. To achieve this goal, the crude oil is subjected to a series of operations and processes. Due to their high amount of impurities (particularly sulfur), straight-run distillates cannot be used directly as fuels; in addition, they possess octane and cetane numbers (naphtha and gas oil, respectively) that are not appropriate for engines. To convert them into suitable materials for fuel production, they need certain treatment, which is carried out in different refining processes. The following sections present a brief description of the main processes used in a petroleum refinery (Ancheyta, 2011, 2013):

1.2.1 Desalting

The first separation process that takes place at the front end of a petroleum refinery is desalting. Its main objective is to prevent corrosion and fouling of downstream lines and equipment by significantly reducing the salt content of oil. Desalting is normally considered a part of the crude distillation unit since heat from some of the streams in the atmospheric distillation is used to heat the crude in the desalting process. Sodium, calcium, and magnesium chlorides, in the form of crystals or ionized in the water present in the crude, are the most frequently found salts in crude oil. The high temperatures found during crude oil refining could cause water hydrolysis if salt is not removed, forming hydrochloric acid (HCl), which will provoke serious corrosion problems in the equipment. Nonremoved salt can also cause fouling problems in pipes, heat transfer equipment, and furnace. Deactivation of catalysts, for example, zeolite-type catalysts used in fluid catalytic cracking (FCC), may be enhanced by metals from salts, particularly sodium. The maximum allowed salt content in the feed to crude distillation units is typically 50 PTB (pounds of salt per thousand barrels of crude oil).

Desalting can be carried out in single stage (dehydration efficiency of ~95%) or in two (dehydration efficiency of ~99%) stages. Dehydration efficiency can be compared with desalting efficiency as most of the salt passed from the organic phase into the water phase if mixing is good. The decision of single or double stage depends on the requirements of the refinery. Typical desalters have an arrangement of two electrodes that generate an electric field among the emulsion causing the droplets vibrate, migrate, and collide with each other and coalesce.

Apart from removing salt, electrostatic desalting also eliminates water and suspended solids in crude oil. Water removal is important to reduce pumping costs and to avoid its vaporization when passing through the preheat train; otherwise, due to high pressure it causes disturbances and vibrations and eventually plant shutdown.

1.2.2 Atmospheric or Primary Distillation

The objective of the atmospheric distillation unit is to fractionate the crude oil into various distillates based on their boiling point ranges. It operates at slightly above atmospheric pressure. The separation is done in a large tower with a number of trays where hydrocarbon gases and liquids interact. The heated desalted crude enters the fractionation tower in a lower section called the flash zone. The unvaporized portion of the crude leaves the bottom of the tower via a steam stripper section, while the distillate vapors move up the tower countercurrent to a cooler liquid reflux stream.

The cooling and condensing of the distillation tower overhead are provided partially by exchanging heat with the incoming crude oil and partially by either an air-cooled or water-cooled condenser. Additional heat is removed from the distillation column by a pump around system, which is simply an internal condenser that ensures a continued reflux stream flow. The overhead distillate fraction from the distillation column is naphtha, which is allowed for leaving the top of the tower to be condensed and collected in the overhead drum. A portion of this stream is returned as reflux, while the rest is delivered to the light end processes for stabilizing and further distillation. The other fractions removed from the side of the distillation column at various points between the column top and bottom are straight-run jet fuel, kerosene, light gas oil, and heavy gas oil, which are steam stripped, cooled by exchanging heat with the incoming crude oil, and sent to other treatments and/or storage. The heavier material, that is, atmospheric residue, is withdrawn from the bottom of the tower. It is important not to subject the crude oil to temperatures above 370–380 °C because high-molecular-weight components will undergo thermal cracking and form coke.

1.2.3 Vacuum or Secondary Distillation

The main objective of a vacuum distillation unit is to recover additional distillates from atmospheric residue. The atmospheric residue is distilled to provide heavy distillate streams used for producing lube oil or as feed to conversion units. The primary advantage of vacuum distillation is that it allows for distilling heavier materials at lower temperatures than those that would be required at atmospheric pressure, thus avoiding thermal cracking. Vacuum distillation is often integrated with atmospheric distillation as far as heat transfer is concerned, which is called combined distillation. Generally, the atmospheric residue is received hot from the atmospheric distillation unit and is sent to the fired heater of the vacuum unit. The vacuum distillation unit is operated at a slight vacuum, which is most often achieved by using multiple stages of steam jet ejectors (absolute pressures as low as 10–40 mmHg). Atmospheric residue is separated into light vacuum gas oil, heavy vacuum gas oil, and vacuum residue.

1.2.4 Solvent Extraction and Dewaxing

Solvent extraction and solvent dewaxing usually remove impurities such as sulfur and nitrogen by dissolving or precipitating at intermediate refining stages or just before sending the product to storage. An important application is the removal of heavy aromatic compounds from lubricating oils. The usual solvents for extraction of lubricating oil are phenol, furfural, and cresylic acid. Solvent dewaxing is used to remove wax from either distillate or residua at any stage in the refining process. Usually two solvents are used: toluene to dissolve the oil and maintain fluidity at low temperatures and methyl ethyl ketone (MEK) to dissolve little wax at low temperatures and act as a wax-precipitating agent. In addition, there is a catalytic process used as an alternative to solvent dewaxing.

1.2.5 Deasphalting

Solvent deasphalting (SDA) is a nondestructive liquid–liquid extraction process (molecular-weight-based separation process), which separates the residue into several fractions on the basis of relative solubility in a solvent (light hydrocarbons such as propane, butane, pentane, or hexane), whereby the last of the molecules that can be refined to valuable products are extracted from the vacuum residue. The application of SDA process has been reported for the production of lube oil feedstocks from vacuum residue using propane as solvent, for the preparation of feedstocks for catalytic cracking, hydrocracking, and hydrodesulfurization (HDS) units, as well as for the production of specialty asphalts. In most of these conversion units, the performance of the catalyst is greatly affected by the presence of heavy metals and the high Conradson carbon content of the residue feed, which are concentrated in asphaltene molecules, so that removing asphaltenes also eliminate these impurities.

SDA process produces a low-contaminant deasphalted oil (DAO) rich in paraffinic-type molecules, and a pitch product rich in aromatic compounds and asphaltenes containing the majority of the feed impurities. The separation of the DAO phase and the pitch phase occurs in an extractor. The extractor is designed to efficiently separate the two phases and minimize contaminant entrainment in the DAO phase. At a constant solvent composition and pressure, a lower extractor temperature increases the DAO yield and decreases the quality. While an increase in solvent ratio the DAO yield remains constant and improves the degree of separation of individual components and results in the recovery of a better quality DAO. The solvent recovered under low pressure from the pitch and DAO strippers is condensed and combined with the solvent recovered under high pressure from the DAO separator, which is then recycled to the initial stage. The produced DAO has lower carbon residue and metal content than the untreated oil; however, SDA is not so effective in lowering sulfur or nitrogen content in DAO.

SDA is also used in refineries to upgrade heavy bottoms streams to DAO that may be processed to produce transportation fuels. The process may also be used in the oil field to enhance the value of heavy crude oil before it gets to the refinery. Thus, SDA is an economically attractive and environmentally friendly process to upgrade heavy petroleum.

1.2.6 Gas and Liquid Sweetening

Gas sweetening is a process used to remove hydrogen sulfide and carbon dioxide from the refinery gas streams. Gas sweetening is generally done with an amine gas treating process, which uses aqueous solutions of various alkanolamines, being MEA (monoethanolamine), DEA (diethanolamine), and MDEA (methyldiethanolamine) the most commonly used amines. MEA has become commercially the most preferred amine due to its high acid gas absorbency.

Apart from amine gas treating, hot potassium carbonate (Benfield) is another process that can be used for acid gas sweetening. There are also other alternatives based on physical solvent processes (Sulfinol, Selexol, Propylene Carbonate, and Rectisol) and dry adsorbents processes (molecular sieve, activated charcoal, iron sponge, and zinc oxide).

Liquid sweetening aims at the elimination of unwanted sulfur compounds (hydrogen sulfide, thiophene, and mercaptans) from crude oil liquid fractions (gasoline, jet fuel, and kerosene) at an intermediate stage in the refining process or just before sending them to storage to improve color, odor, and oxidation stability. The most common process to achieve this target is Merox (mercaptan oxidation). Acids, solvents, alkalis, oxidizing and adsorption agents are the most common materials used for liquid sweetening.

1.2.7 Sour Water Treatment

Sour water (water that contains hydrogen sulfide, ammonia, phenol, and cyanide) is typically treated by a stripping unit with steam whereby H_2S and NH_3 are released at the top of the stripping tower. The H_2S-free water is treated in a biological wastewater treatment plant, where the remaining ammonia is nitrified and then denitrified. In a typical stripping unit, the sour water is fed on the top tray of the tower while steam is introduced below the bottom tray, lending themselves to tray-by-tray mass and heat transfer. The sour water stripping unit is almost always located in the process area of the refinery and can be a single tower with no reflux or a single trayed tower with an overhead reflux stream. Other processes for treatment of sour water are caustic/acid neutralization, caustic oxidization, and oil removal by settling.

1.2.8 Catalytic Reforming

Catalytic reforming is used to convert low-octane straight-run naphtha into high-octane gasoline, called reformate, and to provide aromatics (BTX: benzene, toluene, and xylene) for petrochemical plants. The reformate has higher content of aromatics and cyclic hydrocarbons. By means of catalytic reforming, the feed is restructured and cracked to produce a product with hydrocarbons of more complex molecular shapes, whose overall effect is the production of a reformate with higher octane numbers than the feed.

Catalytic reforming also produces very significant amounts of hydrogen gas as by-product, which is released during the catalyst reaction and is used in other processes within the refinery, for example, catalytic hydrotreating (HDT) and hydrocracking.

1.2.9 Isomerization

Isomerization produces gasoline blending component from light paraffins. The objective of isomerization is to convert low-octane *n*-paraffins to high-octane isoparaffins by using a chloride-promoted fixed-bed reactor. As a result of the isomerization reactions, highly branched, high-octane paraffinic blending components are obtained, which by themselves can satisfy the strictest gasoline environmental requirements.

However, the production of this isomerate is low and other streams for gasoline blending are still necessary. Isomerization of *n*-butane is also one of the sources for the isobutane required in alkylation.

1.2.10 Alkylation

The objective of the alkylation process is to combine light olefins (primarily a mixture of propylene and butylene) with isobutane to form a high-octane alkylate gasoline (highly branched C_5–C_{12} isoparaffins), whose major constituents are isopentane and isooctane (2,2,4-trimethyl pentane) with an octane number of 100. Alkylation is an important process that enhances the yield of high-octane gasoline. The reaction occurs in the presence of a highly acidic liquid catalyst (HF: hydrofluoric acid or H_2SO_4: sulfuric acid). As a consequence of the environmental problems associated with the use of these liquid catalysts, solid acid catalysts have also been proposed, with the major problem of rapid deactivation due to coke formation. The function of the acid catalyst is to protonate the olefins feed to produce reactive carbocations, which alkylate isobutane. Alkylation reaction occurs with 100% olefin conversion. It is important to keep a high isobutene-to-olefin ratio to prevent side reactions, which can produce a lower octane product. This is the reason why alkylation units have a high recycle of isobutane.

1.2.11 Polymerization

The objective of a polymerization unit is to combine or polymerize propylene and butylene into molecules of two or three times their original molecular weight. The feeds to this process are propane and butane produced by catalytic cracking. The produced polymer gasoline has an octane number greater than 90 and is an important part of a refinery since polymerization process increases the yield of gasoline possible from gas oil. The polymerization reaction consists of passing the C_3–C_4 hydrocarbon stream with a high proportion of olefins through a reactor containing a phosphoric-acid-supported catalyst, where the carbon–carbon bond formation occurs.

1.2.12 Catalytic Hydrotreating

Catalytic HDT is one of the most important processes in the petroleum refining industry. It is applied to treat almost all of the refinery streams, from straight-run distillates to vacuum residua. The main differences of the HDT processes of each feed are the operating conditions, type of catalyst, reactor configuration, and reaction system. Depending on the feed and the main objective of the treatment, the process can be called HDS, as in the case of straight-run naphtha, which is used as reforming feed where sulfur is the main undesirable heteroatom; HDT for straight-run gas oil because in addition to sulfur removal, aromatic saturation and nitrogen removal are desired for diesel fuel production; hydrodemetalization for the removal of vanadium and nickel from heavy oils; and hydrocracking to change the molecular weight of heavy feeds.

During HDT a number of reactions are carried out, that is, hydrogenolysis, by which C–S, C–N, or C–C bonds are cleaved, and hydrogenation of unsaturated compounds. The reaction conditions of the HDT process vary with the type of feedstock; while light oils are easy to desulfurize, desulfurization of heavy oils is much more difficult. The HDT reactions take place in catalytic reactors at elevated temperatures and pressures typically in the presence of a catalyst consisting of an alumina base impregnated with cobalt or nickel and molybdenum.

1.2.13 Fluid Catalytic Cracking

The FCC increases the H/C ratio by carbon rejection in a continuous process and is used to convert high-boiling, high-molecular weight hydrocarbon fractions (blend of heavy straight-run gas oil, light vacuum gas oil, and heavy vacuum gas oil) to more valuable gasoline, olefinic gases, and other products. The process consists of two main vessels: a reactor and a regenerator, which are interconnected to allow for transferring the spent catalyst from the reactor to the regenerator and the regenerated catalysts from the regenerator to the reactor. During catalytic cracking, the feed is vaporized and long-chain molecules are cracked into much shorter molecules by contacting the feed with a fluidized powdered catalyst at high temperature and moderate pressure.

According to this mechanism, a catalyst promotes the removal of a negatively charged hydride ion from a paraffin compound or the addition of a positively charged proton (H+) to an olefin compound, which results in the formation of a carbonium ion. Carbonium ion is a positively charged molecule that has only a very short life as an intermediate compound and transfers the positive charge through hydrocarbons. This carbonium transfer continues as hydrocarbon compounds come into contact with active sites on the surface of the catalyst that promote the continued addition of protons or removal of hydride ions. This results in weakening of carbon–carbon bonds in many of the hydrocarbon molecules and consequent cracking into smaller compounds. These formed ions also react with other molecules, isomerize, and react with the catalyst to terminate a chain. Coke formation is unavoidable in the catalytic cracking process, which is likely formed by dehydrogenation and condensation of polyaromatics and olefins. Fast deactivation by blocking the active pores of the catalyst is a consequence of coke deposition. During these reactions, the produced catalytic cracked gasoline contains a large amount of aromatics and branched compounds, which is beneficial for the gasoline octane numbers.

1.2.14 Gasification

This process involves complete cracking of residue, including asphaltenes, into gaseous products. The gasification of residue is carried out at high temperature (>1000 °C), yielding synthesis gas or syngas (consisting primarily of hydrogen, carbon monoxide, carbon dioxide, and water), carbon black, and ash as major products. The syngas can be converted into hydrogen or used by cogeneration facilities to provide low-cost power and steam to refineries.

An integrated SDA-gasification facility is an attractive alternative for upgrading of heavy petroleum. The following are some of the benefits obtained by integrating deasphalting and gasification: heavy oils can be upgraded economically, reduction of capital and operating costs of both processes, higher yields of DAO, lower emissions, and increased profit margins of a refinery.

1.2.15 Coking

There are three main coking processes in use:

1.2.15.1 Delayed Coking Delayed or retarded coking can produce shot coke (a type of fuel coke), sponge coke (used to produce anode coke or as a fuel coke), or needle coke. This process accounts for the majority of the coke currently produced in the world. Delayed coking is a semicontinuous thermal cracking process used in petroleum refineries to upgrade and convert bottoms from atmospheric and vacuum distillation of crude oil into liquid and gas product streams, leaving behind a solid concentrated carbon material, petroleum coke, whose value will depend on its properties such as sulfur and metals. The products of a delayed coker are wet gas, naphtha, light and heavy gas oils, and coke. The coke produced in the delayed coker is almost pure carbon and is utilized as fuel or, depending upon its quality, in the manufacture of anodes and electrodes.

In a delayed coker, the feed enters the bottom of the fractionator, where it mixes with recycled liquid condensed from the coke drum effluent. It is then pumped through the coking heater, then to one of two coke drums through a switch valve. The total number of coke drums required for a particular application depends on the quality and quantity of the feed and the desired coking cycle. A minimum of two drums is required for operation, with one drum receiving the heater effluent while the other is being decoked.

A delayed coking unit is frequently designed with the objective of maximizing the yield of liquid product and minimizing the yield of wet gas and coke. The conversion is accomplished by heating the feed material to a high temperature and introducing it into a large drum to provide soaking or residence time for the three major reactions to take place: partial vaporization and mild cracking (visbreaking) of the feed, thermal cracking, and polymerization.

Delayed coking has been selected by many refiners as their preferred choice for upgrading of bottom of the barrel, because of the process's inherent flexibility to handle any type of residua. The process provides essentially complete rejection of metals and carbon while providing partial conversion to liquid products (naphtha and gas oil).

The product selectivity of the process is based on the operating conditions, mainly pressure and temperature. This process is more expensive than SDA, although still less expensive than other thermal processes. The disadvantages of this process are very high coke formation and low yield of liquid products. Despite these disadvantages, delayed coking is the most preferred process for all refiners for residue processing. Advances in delayed coking (low pressure, low oil recirculation) have increased the production of light products and reduced the production of coke.

1.2.15.2 Fluid Coking Fluid coking produces fluid coke typically used as fuel coke. It is a continuous process that uses the fluidized-solids technique to convert residue feedstock into more valuable products. The heated coker feeds (petroleum residua) are sprayed into a fluidized bed of hot, fine coke particles, which are maintained at 20–40 psi and 500 °C. The use of a fluid bed permits the coking reactions to be conducted at higher temperatures and with shorter contact times than in delayed coking. These conditions result in lower yields of coke and higher yields of liquid products. Fluid coking uses two vessels, a reactor and a burner. Coke particles are circulated between these vessels to transfer heat to the reactor. This heat is generated by burning a portion of the coke. The reactor contains a fluidized bed of coke particles, which is agitated by the introduction of steam at the bottom. The residue feed is injected directly into the reactor and is distributed uniformly over the surface of the coke particles, where it cracks and vaporizes. The feed vapors are cracked while forming a liquid film on the coke particles. The particles grow by layers until they are removed and new seed coke particles are added. Coke is a product and a heat carrier.

1.2.15.3 Flexi-Coking Flexi-coking produces a type of fluid coke that is gasified to generate a low-BTU synthesis gas. It is an extension of fluid coking, which includes the gasification of the coke produced in the fluid coking operation and produces syngas, but the temperature (1000 °C) used is insufficient to burn all coke.

Both fluid coking and flexi-coking are fluid bed processes developed from FCC technology. In both processes, the circulating coke carries heat from the burner back to the reactor, where the coke serves as reaction sites for the cracking of the residua into lighter products. Fluid coking can have liquid yield credits over delayed coking. The shorter residence time can yield higher quantities of liquids and less coke, but the products have lower quality. Fluid coking is a slightly better process than delayed coking because of the advantage of a slightly improved liquid yield, also because delayed coking has higher utilities cost and fuel consumption.

1.2.16 Visbreaking

Visbreaking (viscosity reduction or breaking) is a mature process that may be applied to both atmospheric (AR) and vacuum (VR) residua and even solvent deasphalted pitch, which by means of a mild thermal decomposition, viscosity is improved. The thermal conversion of the residue is accomplished by heating at high temperatures in a specially designed furnace. A common operation is to visbreak residue in combination with a thermal cracker to minimize fuel oil while producing additional light distillates. Visbreaking is a process in which residue stream is heated in a furnace (450–500 °C) and then cracked during a low specific residence time, to avoid coking reactions within a soaking zone under certain pressure and moderate temperature conditions. The cracked product leaves the soaking zone after the desired conversion is achieved and then quenched with gas oil to stop the reaction and prevent coking. The residence time, temperature, and pressure of the furnace's soaking zone is controlled to optimize the thermal free radical cracking to produce the desired products. In general, visbreaking is used to increase the refinery net distillate yield.

The main objectives of visbreaking are to reduce the viscosity of the feed stream and the amount of residual fuel oil produced by a refinery and to increase the proportion of middle distillates in the refinery output.

1.2.17 Residue Fluid Catalytic Cracking (RFCC)

Residue fluid catalytic cracking (RFCC) is an extension of conventional FCC technology that was developed during the early 1980, which offers better selectivity to high gasoline and lower gas yield than hydroprocessing and thermal processes. The RFCC process uses similar reactor technology to the FCC process, in which the catalyst is in fluidized bed at a temperature of 480–540 °C, and is targeted for residual feeds greater than 4 wt% Conradson carbon. Because RFCC requires better feed quality (e.g., high H/C ratio, low content of metals and asphaltenes), it makes this process less likely than hydroprocessing. The need of good feedstock quality is to avoid unreasonable high coke yield, high catalyst consumption, and unit operability. However, such feeds are high in price and limited in refineries.

To control heat balance and to recover part of the heat for steam production, RFCC process design includes two-stage regeneration, mix temperature control, and catalyst cooler. The catalyst properties also play an important role in resisting metal content and carbon deposition. In this respect, catalyst pore structure limits the diffusion of residue on the catalytic sites. The catalyst used for RFCC is of acidic matrix such as crystalline aluminosilicate zeolite in inorganic matrix, which exhibits the required physical–chemical properties.

1.2.18 Hydrovisbreaking Process

1.2.18.1 HYCAR This is one kind of noncatalytic processes, which is based on visbreaking and involves treatment with hydrogen at mild conditions. This process is completed in three reactors: (1) visbreaking, a moderate thermal cracking process in the presence of hydrogen, which leads to more stable products than those obtained with straight visbreaking; (2) hydrodemetalization, which removes impurities particularly metals, before sending to the next reactor; and (3) hydrocracking, where desulfurization and denitrogenation take place along with hydrocracking.

1.2.18.2 Aquaconversion It is a catalytic process that uses catalyst-activated transfer of hydrogen from water added to the feedstock in slurry mode. The homogeneous catalyst is added in the presence of steam, which allows the hydrogen from the water to be transferred to the heavy oil when contacted in a coil–soaker system normally used for the visbreaking process. Reactions that lead to coke formation are suppressed and there is no separation of asphaltene-type material.

The presence of the oil-soluble catalyst and water prevents the coke formation and deposition of sediment that often occurs during visbreaking. In this process, the catalyst may be used as a support or mixed directly with the feedstock. The metals (metal salts) used for hydrovisbreaking are alkali metals such as potassium or sodium. The role of the catalyst is to enhance the dissociation of H_2O to release hydrogen (H^+) ions, which are subsequently consumed in hydroprocessing.

1.2.19 Fixed-Bed Hydroprocessing

Hydroprocessing of residue in fixed-bed reactor (FBR) is well established and reported in the literature. The general characteristic of hydroprocessing is the simultaneous or sequential hydrogenation of hydrocarbon feed in the presence of sulfided catalyst by reacting with hydrogen. The main problem with fixed-bed catalyst is deactivation over time, which can be minimized by a guard-bed reactor, in order to reduce the metal deposition on the downstream reactors. Several combinations using two or three processing steps can be implemented in the refining. The catalyst in the guard-bed reactor is typically an HDM catalyst or large pore catalyst with high metal-retention capacity. Various improvements have been reported in the past decade to increase efficiency of fixed-bed hydroprocessing such as run length, conversion, and product quality. Some of these improvements have been focused on mechanical design such as the use of bunker, swing reactors, guard-bed reactors, feed distribution, coke and metal deactivation resistant catalyst, including pore and particle grading and onstream catalyst replacement. In spite of all disadvantages, mainly short catalyst life, up until now most of residue hydroprocessing units have FBRs. The representative technologies of fixed-bed hydroprocessing are RDS/VRDS, Hyvahl-F and Hyvahl-S, IFP hydrocracking process, Isocracking, Mild hydrocracking, MRH Process, Unicracking Process (Unicracking, APCU: Advanced Partial Conversion Unicracking, HyCycle Unicracking Technology), and HIDRO-IMP.

1.2.20 Moving-Bed Hydroprocessing

There are a few types of hydroprocessing reactors with moving catalyst beds, in which the catalyst goes in downflow through the reactor by gravitational forces. In general, catalyst replacement is a batch operation, which is done typically once or twice a week. The fresh catalyst enters at the top of the reactor and the deactivated catalyst leaves the reactor at the bottom, while the hydrocarbon goes either in counter- or cocurrent flow through the reactor. With this moving-bed reactor (MBR), the catalyst can be replaced either continuously or in batch operation. Catalyst transfer is the most critical section. Countercurrent mode of operation seems to be the best configuration since the spent catalyst contacts the fresh feed at the bottom of the MBR, while the fresh catalyst reacts with an almost already hydrodemetalized feed at top of the MBR, resulting in lower catalyst consumption. The moving-bed hydroprocessing technologies are HYCON process, OCR process (Onstream Catalyst Replacement), Hyvahl-M.

1.2.21 Ebullated-Bed Hydroprocessing

In ebullated-bed hydroprocessing, the catalyst within the reactor is not fixed. In such a process, the hydrocarbon feed stream enters the bottom of the reactor and flows upward through the catalyst, which is kept in suspension by the pressure of the fluid feed. The hydrocarbon feed and hydrogen are fed upflow through the catalyst bed, expanding and backmixing the bed, minimizing bed plugging and ΔP. The oil is separated from the catalyst at the top of the reactor and recirculated to the bottom of the bed to mix with the new feed. On the other way, fresh catalyst is added to the top of the reactor and spent catalyst is withdrawn from the bottom of the reactor.

Ebullated-bed reactors (EBR) are capable of converting the most problematic feeds, such as AR, VR, and all other heavy oil feedstocks, which have high content of asphaltenes, metals, and sulfur. Ebullating bed reactors can perform both HDT and HCR functions; thus, these reactors are referred as dual-purpose reactors. Ebullating bed catalysts are made of pellets or grains that are less than 1 mm in size to facilitate suspension by the liquid phase in the reactor.

There are three main ebullated-bed processes, which are similar in concept but different in mechanical aspects: H-Oil, T-Star, and LC-Fining.

1.2.22 Slurry-Bed Hydroprocessing

Slurry-bed reactor (SBR) can also be used for hydroprocessing of feeds with very high metal content to obtain lower boiling products using single reactor. SBR-based technologies combine the advantages of the carbon rejection technologies in terms of flexibility with the high performances peculiar to the hydrogen addition processes. SBR achieves a similar intimate contacting of oil and catalyst and may operate with lower degree of backmixing than EBR. Differently to FBR and EBR, in SBR small amount of finely divided powder is used, which can be an additive or a catalyst (or catalyst precursors). The catalyst is mixed with the feed (heavy oil) and both are fed upward with hydrogen through an empty reactor vessel. Since the oil and catalyst flow cocurrently, the mixture approaches plug-flow behavior. In SBR, the fresh catalyst is slurried with the heavy oil prior to entering the reactor, and when the reaction finishes, the spent catalyst leaves the SBR together with the heavy fraction and remains in the unconverted residue in a benign form. The slurry-bed hydrocracking technologies are CANMET, Microcat-RC, MRH, Veba Combi Cracking (VCC), HDH (Hydrocracking Distillation Hydrotreating), and Eni Slurry Technology (EST).

1.3 PROPERTIES OF HEAVY PETROLEUM

This section describes the most important properties of heavy crude oils that affect deactivation of catalysts.

1.3.1 Physical and Chemical Properties

Heavy crude oil is a thick, black, gooey fluid, harder to handle, and more expensive to refine to produce the most valuable petroleum products. Heavy oil is a type of crude oil that is very viscous, meaning that it does not flow easily. The common properties of heavy oil are high specific gravity (low API gravity), low hydrogen-to-carbon ratio, high carbon residue, high content of asphaltenes, heavy metals (mainly V and Ni), sulfur, and nitrogen.

Because heavy oil is deficient in hydrogen compared with conventional crude oil, either hydrogen must be added to the molecules or carbon be removed to render it a useful feedstock for a conventional refinery.

The physical and chemical properties, as well as exact chemical composition, of heavy crude oil vary from one source to another. Crude oils, especially heavy crude oils, contain large quantities of asphaltenes (high-molecular-weight polar components). Other crude oil components are resins, fatty acids such as naphthenic acids, porphyrins, and wax crystals, which can associate to asphaltenes and affect the oil stability. Particles such as silica, clay, and iron oxides can be present in crude oils.

Table 1.2 reports the properties of several heavy crude oils. Heavy crude oils exhibit a wide range of physical and chemical properties. While the properties such as viscosity, density, boiling point, and color may vary widely, the ultimate or elemental analysis varies over a narrow range. The carbon content is relatively constant, while the hydrogen and heteroatom contents are responsible for the major differences. Nitrogen, oxygen, and sulfur can be present in only trace amounts in some heavy crude oils, which consist primarily of hydrocarbons.

It is the heteroelements that can have substantial effects on the distribution of refinery products. Coupled with the changes brought about to the feedstock constituents by refinery operations, it is not surprising that refining heavy feedstocks is a monumental task. Thus, initial inspection of the feedstock (conventional examination of the physical properties) is necessary. From this, it is possible to make deductions about the most logical means of refining. In fact, evaluation of crude oils from physical property data as to which refining sequences should be employed for any particular crude oil is a predominant part of the initial examination of any material that is destined for use as a refinery feedstock.

The chemical composition of a heavy crude oil is a much truer indicator of refining behavior. Whether the composition is represented in terms of compound types or in terms of generic compound classes, it can enable the refiner to determine the nature of the reactions. Hence, chemical composition can play a major part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed.

Thus, initial inspection of the nature of the feedstock will provide deductions about the most logical means of refining or correlation of various properties to structural types present and hence attempted classification of the petroleum. Indeed, a careful evaluation from physical property data is a major part of the initial study of any refinery feedstock. Proper interpretation of the data obtained from the inspection of crude oil requires an understanding of their significance.

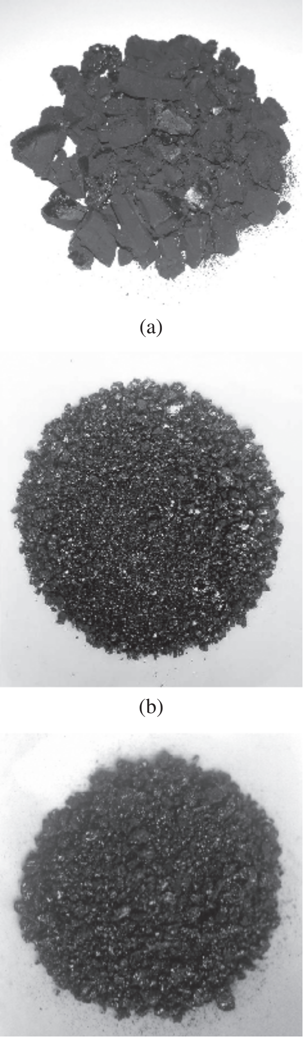
1.3.2 Asphaltenes

A crude oil can be separated into two main components: asphaltenes and maltenes. The heavy fractions of petroleum can be defined as molecules possessing more than

TABLE 1.2 Properties of Different Crude Oils

Country	USA	Venezuela	USA	USA	Kuwait	USA	Canada	USA	Canada
Crude oil	California 11	Boscan	California 15	Beta	Eocene	Hondo	Hebron	Carpinteria	Atkinson
API gravity	10.3	10.9	13.2	13.7	18.6	19.6	20.1	22.9	23.7
Total sulfur (wt%)	3.3	5.5	5.5	3.78	4.55	4.3		1.88	0.86
Viscosity at (cP)									
0 °C	220,000	8,826,000	31,000	90,210		3,507		790	65
15 °C	34,000	485,500	6,400	13,380		735	680	164	
30 °C							185		
SARA analysis (wt%)									
Saturates		25	19			33		44	47
Aromatics		35	35			31		30	36
Resins		22	23			24		17	14
Asphaltenes	16	18	23			12		9	3
Metals (wppm)									
Ni	1,606	117	111	112		75	6	49	2
V	245	1,320	266	146		196	1	112	9
Water content (wt%)	8.6		0.1	1.7		1.5		0.1	
Reid vapor pressure (kPa)					8				6
Pour point (°C)	0	21	−9	3	−29	−15	−4	−21	−46

25 atoms of carbon distributed in polar and heavy compounds, such as asphaltenes and resins, having high boiling points (Merdrignac and Espinat, 2007). Since asphaltenes are the main constituents of heavy crude oils and their structure and composition directly affect the whole composition of the petroleum, they deserve special attention. Figure 1.1 shows the physical aspects of asphaltenes precipitated from various crude oils. Although not very clear, it is observed that asphaltenes from heavy crude oils



(a)

(b)

(c)

Figure 1.1 Asphaltenes precipitated from various crude oils: (a) 13°API, (b) 21°API, and (c) 33°API.

are blacker than those from light crude oils, which indicates more complexity of the former.

The most common and widely accepted definition of asphaltenes is based on their solubility properties (Ancheyta et al., 2010):

"Asphaltenes are insoluble in alkanes such as *n*-pentane, *n*-hexane, *n*-heptane or higher but soluble in aromatic solvents (i.e., benzene, toluene)."

The asphaltene content is mostly reported as *n*-heptane insolubles; however, strictly speaking, they must be calculated as the difference between weight percentage of *n*-heptane insolubles and the weight percentage of toluene insolubles.

Asphaltenes are commonly precipitated from crudes by adding *n*-heptane because their properties do not exhibit significant changes when using *n*-heptane or higher carbon number alkanes (Andersen, 1994).

Asphaltenes are the main precursors of sludge or sediments. They are polyaromatic complex compounds with a boiling point higher than 500 °C, which have the following components: aromatic rings carrying alkyl chains up to C_{30}; sulfur present in benzothiophene rings and nitrogen contained in pyrrol and pyridine; ketones, phenols, carboxylic acids; nickel and vanadium complexed with pyrrole nitrogen atoms in porphyrinic rings.

The other component of a crude oil, maltenes, has the following constituents: resins, which are structures similar to asphaltenes but having lower molecular weight; oxygen, nitrogen, and sulfur are not always present in aromatic structures; naphthenes and other saturate hydrocarbons such as straight or branched chains.

The complexity of heavy oils makes compositional analysis very complex, and separation is carried out for compound types instead of individual compounds. When more insolubles (asphaltenes) are removed, the soluble fraction (maltenes) is rich in hydrogen. Sulfur, nitrogen, and oxygen of soluble fractions decrease as more insolubles are removed. Typically, the insoluble fraction contains 7–21 heteroatoms per molecule, and the soluble fraction has 0.8–1.7 (Sharma et al., 2007).

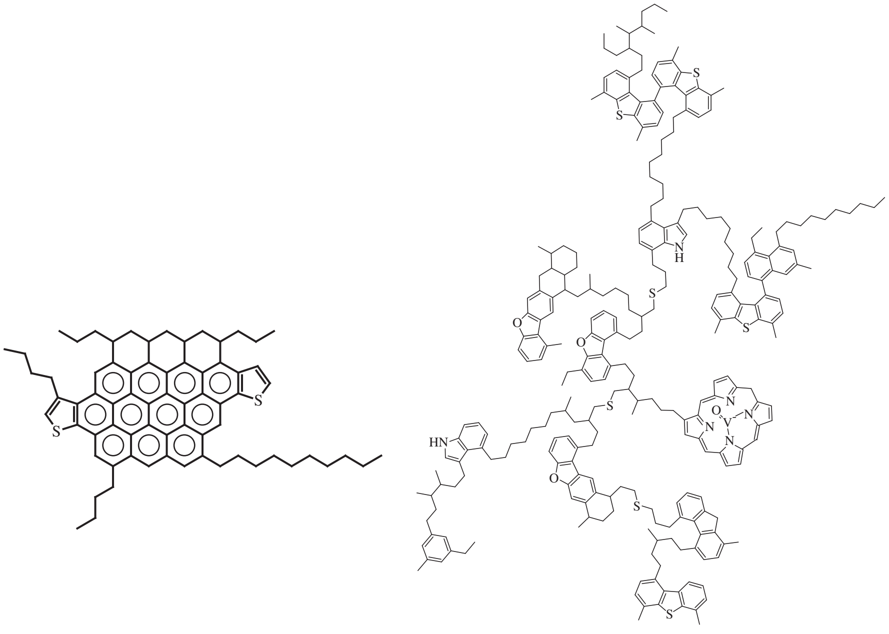
Asphaltenes can be modeled in two different ways:

- Continental type, pericondensed structures in which asphaltene cores are constituted by more than seven aromatic rings.
- Archipelago type, in which asphaltenes are represented by small aromatic cores linked to other cores by means of bridging alkanes, that is, presence of islands of small aromatic cores linked by alkyl and sulfur bonds.

Hypothetical structures of these two asphaltene types are presented in Figure 1.2 (Zhao et al., 2001). The way in which both types of asphaltenes aggregate is different. Archipelago-type asphaltenes form planar aggregates in asphaltenes solutions, whereas continental-type asphaltenes are able to stack forming columns (Murgich et al., 1996).

1.3.3 Tendency to Coke Formation

The tendency to coke formation of crude oils is commonly measured with two analyses: Ramsbottom carbon and Conradson carbon residue. Matsushita et al. (2004)



(a) (b)

Figure 1.2 Hypothetical structures of asphaltenes: (a) Continental type and (b) Archipelago type.

also defined the following relationship that takes into account the H/C atomic ratio of asphaltenes and maltenes, which gives certain information about the solubility of asphaltenes and its influence on coke formation during processing of petroleum:

$$\text{Relative solubility index (RSI)} = \frac{\mathrm{H/C\ of\ asphaltenes}}{\mathrm{H/C\ of\ maltenes}} \tag{1.3}$$

It was reported that the higher the relative solubility index, the lesser the coke formation and that at lower RSI more coke will be deposited, which will have less H/C (more aromatic coke). Based on this index, asphaltenes and maltenes from three crude oils were precipitated and characterized by elemental analysis, and RSI was calculated. The results are presented in Figure 1.3. It can be anticipated that heavy crude oils will have more tendency to form coke during their processing.

1.3.4 Viscosity of Crude Oils and Blends

The problem of determining the viscosity of heavy crude oils is not so critical since most of the times a viscometer is always available in the laboratory. However, sometimes it is required to calculate viscosity of either crude oils or blends of crude oils.

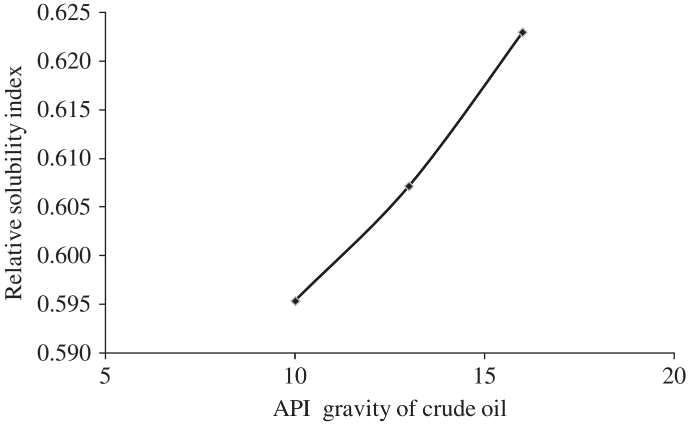


Figure 1.3 Tendency to coke formation of crude oils.

Various standardized methods are available for experimental determination of viscosity for different types of crudes and petroleum products. The most used are ASTM D88, ASTM D445, ASTM D2170, ASTM D7042, ASTM D7483, and ASTM E102. The major differences among them are the type and required amount of sample, experimental setup, time for analysis, operating conditions of equipment, and ranges of viscosity in which the device can be used. In practice, it has been observed that measuring the viscosity of crude oils with low API gravity is complicated due to their own nature and difficulty to handle. This makes the analysis requires more time and greater amount of sample to obtain reliable results.

1.3.4.1 Viscosity of Crude Oils Viscosity is the most important property used for defining if a crude oil is suitable for transportation. In general, heavy crude oils (low API gravity) exhibit high viscosity. As was already stated, the common specification for crude oil transportation is a maximum viscosity of 250 cSt at 100 °F and a minimum API gravity of 16° (Hedrick et al., 2006).

The viscosity of crude oil can be predicted by means of correlations. Several methods have been proposed to predict dead oil viscosity (μ_{od}), saturated or bubble point viscosity (μ_{ob}), and undersaturated oil viscosity (μ_o). Depending on the category, the correlation uses parameters and properties such as API gravity, temperature, pour point, pressure, bubble point pressure, gas–oil ratio, and molecular weight. According to this, two types of correlations for the prediction of crude oil viscosity are reported in the literature: (1) those using conditions and bulk properties such as temperature, pressure, and specific gravity and (2) those using crude oil composition, normal boiling point, and pour point temperature.

All authors reported high accuracy for viscosity prediction with their correlations; however, they were developed and tested with a particular set of experimental data, and extrapolation to other data may change the precision of predictions.

Sánchez et al. (2014) compared the correlations developed to predict the dynamic viscosity of crude oil as a function of API gravity and temperature. The most used correlations have been developed by Beal, Beggs, Glaso, Egbogah, Kartoatmodjo, Elsharkawy, Naseri, Hossain, Alomair, and Petroski (Sánchez et al., 2014). Some of the equations exhibit similarities in the number of parameters included (e.g., Egbogah and Elsharkawy) or in the mathematical structure, such as Beggs and Egbogah (with an additional parameter in the correlation proposed by Beggs). Moreover, Glaso and Kartoadmodjo coincide in using the API gravity value raised to an exponent that depends on the temperature. However, the equations proposed by Kartoadmodjo, Hossain, and Alomair reach higher viscosity values, therefore applicable for heavy crude oils.

Even though the authors of correlations claim that accurate predictions can be obtained with their proposed equations, the correlation usually will not work for a crude oil with different API gravity and temperature range from those that were used to develop it.

The authors used 12 crude oils with a wide range of API gravity (12.4–43°API) for comparison of correlations. It was found that all correlations tend to fail as the viscosity values increase, that is, for heavy oil samples, so that an accurate correlation was needed for calculating viscosity of heavy crude oils. Thus, a new correlation involving two coefficients that are functions of API gravity was proposed, which was validated using viscosity values different from those used to derive it. A comparison of results using literature information and own set of data indicated better predictability over other correlations previously reported. The developed correlation presents a good performance in the range of API gravity evaluated (12.4–43.0°). However, its higher precision was observed for API gravity lower than 21.1°, even higher than other correlations reported in literature. Therefore, the following proposed correlation is recommended to predict the viscosity of heavy and extra-heavy crude oils (Sánchez et al., 2014):

$$\mu = a\exp(b/T^3) \tag{1.4}$$

$$a = 3.9\times10^{-5}\,\mathrm{API}^3 - 4.0\times10^{-3}\,\mathrm{API}^2 + 0.1226\,\mathrm{API} - 0.7626 \tag{1.5}$$

$$b = 9.1638\times10^{9}\,\mathrm{API}^{-1.3257} \tag{1.6}$$

where μ is the dynamic viscosity in centipoise, T the absolute temperature in Kelvin, and a and b are coefficients, which depend on API gravity.

1.3.4.2 Viscosity of Blends of Crude Oils Crude oil blending is often undertaken to increase the sale price or processability of a lower grade crude oil by blending it with a higher grade, higher price crude, aiming at producing blended crude oil to a target specification at the lowest cost using the minimum higher cost crude oil.

Refiners usually want to know in advance which crude oils should be mixed and in which volumetric ratios, in order to achieve the desired value of viscosity or of other properties. Thus, the prediction of viscosity of crude oil blends becomes a mathematical issue rather than experimental. That is done with the help of mixing rules.

A total of 26 mixing rules are reported in the literature (Centeno et al., 2011), which can be classified according to the number and type of parameters involved for the calculation of viscosity, as well as experimental information required.

- *Pure Mixing Rules*. Pure mixing rules are easy to apply as they only require experimental viscosity of components and composition of mixtures in terms of volume or weight fractions, such as the Arrhenius, logarithmic, Bingham, Kendall, and Monroe, linear, Cragoe, Reid, and Chirinos.
- *Mixing Rules with Viscosity Blending Index*. These rules were developed to predict blend viscosities of all petroleum components from gasoline to vacuum residue. The Refutas index method belongs to this classification, which uses the Refutas index of each component (VBI_i: Viscosity Blending Index or Viscosity Blending Number) and the Refutas index of the blend (VBI_β). The Chevron equation is another example of mixing rule that involves calculation of VBI_β.
- *Mixing Rules with Additional Parameters*. This type of mixing rules includes calculation of extra parameters that are usually obtained by mathematical methods. Among these rules are those proposed by Walther, Latour, Lederer, Shu, Ishikawa, Lobe, power law, Barrufet, and Setiadarma, ASTM D341 method optimized by Twu and Bulls, Panchenkov, Reik, and Lima.
- *Mixing Rules with a Binary Interaction Parameter*. Expressions for estimating viscosity that include a binary interaction parameter have been proposed by several authors such as Van der Wyk, Grunberg and Nissan, and Tamura and Kurata. McAllister proposed a method involving two interaction parameters that are calculated from known values of the mixture viscosity. According to this method, the interaction parameters vary linearly with the inverse of temperature; thus, if the values of these quantities are known at two temperatures, it should be possible to read the values at other temperatures from appropriate graphs.
- *Mixing Rules with an Excess Function*. Ratcliff and Khan calculated the viscosity of a mixture based on the absolute viscosities of components; it is necessary to include an excess function to account for deviation from ideality. Wedlake and Ratcliff reported a model based on an excess quantity that is calculated from a structural constant, the number of groups in molecular species, and the individual group contribution of each group in the mixture.

Mixing rules range from that purely empirical to those that require detailed experimental information and to solve relatively complex mathematical functions. The pure mixing rules are the simplest of the rules. They have been widely used precisely by its simplicity and little experimental information needed (only data of viscosity and proportion of the blend components). This type of mixing rules has a basic mathematical structure (e.g., linear, logarithmic, inverse, power law) that oversimplifies the problem, so their successfulness in predicting viscosity of heavy oils is nearly random. The mixing rules with additional parameters try to compensate the simplicity of the pure mixing rules by adding constants, which in fact are correlation parameters whose values have been calculated from experimental data and are valid only within the range of conditions used for their determination. The authors of these rules claim more accurate results than the pure mixing rules, which is expected, as the number of parameters increases how well a correlation fits the data is also better.

It is well known that viscosity does not blend linearly, but a function of viscosity, the Viscosity Blending Index, does. Blending linearly means that the value of viscosity of a blend is simply the arithmetic mean of the values of viscosity for the components weighted by the quantity of the component in the blend. The mixing rules based on VBI (Refutas and Chevron) should, in principle, behave better for predicting viscosity. This indeed happens but only for low-viscosity samples. The reason behind this underperformance is because viscosity is a nonadditive property that behaves differently from those based on mass, such as impurity content and density.

The mixing rules with a binary interaction parameter or with an excess function are supported by thermodynamic concepts and may achieve better performance than the others. In any case, the parameters have to be estimated from a wide range of experimental data and blends, so that the application of these mixing rules can be extended to other samples different from those used to derive the parameter values.

It is worth to mention that petroleum is generally close to Newtonian fluids; however, it strongly depends on oil composition. It is quite likely that at low temperatures the oil is so viscous that Reynolds number drops drastically (by virtue of the log–log relationship). Viscosity variability is more related to composition than density/temperature. Due to this, viscosity is one of the most unreliable properties to determine by equations. Commercial process simulators offer several correlations, but they are usually not accurate for heavy oils.

Centeno et al. (2011) concluded that the pure mixing rules estimate crude oil viscosity with high standard error. The most-known and used Refutas and Chevron mixing rules show general overestimation of experimental viscosity, while only those rules that include an additional parameter such as the Walther, Einstein, and power law predict viscosity with relative low error. No rule shows capability to accurately estimate the viscosity for all crude oils, as the disagreement of estimated and experimental values increased with the API decrement. The analysis of light petroleum distillate blends confirms that the capability of each mixing rule to predict viscosity decreases as the sample becomes heavier. The results show that predicting viscosity of heavy crude oils and their blends is still a challenging task, and a proper mixing rule for such a purpose is needed.

More recently, Centeno et al. (2015) also examined the method developed by Ratcliff and Khan for calculating viscosity of crude oil blends by using data from the literature. To apply this method, it is necessary to include an excess function to account for deviation from ideality, by means of the following equation:

$$(\ln \nu)_{\text{real}} = \sum x_i \ln \nu_i \pm (\ln \nu)^E \tag{1.7}$$

where the excess function is defined by

$$(\ln \nu)^E = a_{\text{AB}} w_{\text{A}} w_{\text{B}} \tag{1.8}$$

For instance, for ternary mixtures, there are three possible combinations for binary blends, that is, three parameters to be estimated: a_{12}, a_{13}, and a_{23}. Applying

Equation 1.8 to this system results in

$$(\ln \nu)_1^E = a_{12}x_1^1x_2^1 + a_{13}x_1^1x_3^1 + a_{23}x_2^1x_3^1 \tag{1.9}$$

$$(\ln \nu)_2^E = a_{12}x_1^2x_2^2 + a_{13}x_1^2x_3^2 + a_{23}x_2^2x_3^2 \tag{1.10}$$

$$(\ln \nu)_3^E = a_{12}x_1^3x_2^3 + a_{13}x_1^3x_3^3 + a_{23}x_2^3x_3^3 \tag{1.11}$$

To solve this system of equations, it is necessary to know the composition of each crude in the blend (x_i^j) and the excess function $(\ln \nu)^E$. (x_i^j) is defined by experimental blends and $(\ln \nu)^E$ can be calculated with the experimental information and Equation 1.7. The authors concluded that in all cases better prediction is obtained with the method using binary interaction parameters. Apart from this, the values of the parameters resulted to have an inverse dependency with temperature, so that a correlation between each parameter with temperature can be established, and viscosity of blends at different temperature can be easily computed.

1.3.4.3 Other Properties Following the same approach described for viscosity of blends, to calculate other properties the following approaches can be used:

1. *Additive Properties*. Those that depend on mass, such as API gravity and impurity content (sulfur, metals, nitrogen), which use the following linear mixing rule:

$$\beta_b = \sum_{i=1}^{N} y_i \beta_i \tag{1.12}$$

   where β_b is the property of the blend, β_i is the property of component "*i*," and y_i is the volume or mass fraction of component "*i*" in the blend.
2. *Nonadditive Properties*. Those that do not depend on mass, such as Reid vapor pressure and flash point. To calculate nonadditive properties, it is necessary to have the blending index of the property, which allows for linearization of the behavior of such a property, by means of the following equation:

$$\mathrm{BI}_b = \sum_{i=1}^{N} y_i \mathrm{BI}_i \tag{1.13}$$

   where BI_i is the blending index of component "*i*."

The following blending indexes are found in the literature for various properties:

Reid vapor pressure (RVP): $\mathrm{BI}_{\mathrm{RVP}} = (\mathrm{RVP})^{1.25}$ (1.14)

Flash point (FP): $\log_{10}\mathrm{BI}_{\mathrm{FP}} = -6.1188 + \dfrac{2414}{\mathrm{FP} - 42.6}$ (1.15)

Pour point (PP): $\mathrm{BI}_{\mathrm{PP}} = \mathrm{PP}^{1/0.08}$ (1.16)

Aniline temperature (AT): $\mathrm{BI}_{\mathrm{AT}} = 1.124[\exp(0.00657 * \mathrm{AT})]$ (1.17)

1.3.5 Stability and Compatibility

The definitions of stability/instability and compatibility/incompatibility are as follows:

- *Stability*. Ability of the oil to remain in an unchanged condition despite circumstances that may tend to cause change, while instability is the tendency of a crude oil to produce a deposit of asphaltenic sludge as a function of time and/or temperature.
- *Compatibility*. Degree to which two or more crude oils of different origins can be mixed without causing flocculation (precipitation) of asphaltene or wax deposition. As a general rule, crude oils of the same type are always compatible. However, even within the same group or type of crude oil, incompatibility can occur. In such cases, the prediction of incompatibility problems requires considerable experimental work.

Once precipitated, it is difficult to redissolve asphaltenes quickly. Meanwhile, precipitated asphaltenes can cause stable oil–water emulsions, plugging of transportation lines, fouling of heat exchangers, and catastrophic coking of distillation furnace tubes.

To be considered as stable and compatible, a blend of various crude oils must have the following characteristics:

- Must be homogeneous immediately after preparation
- Must remain homogeneous in normal storage
- Must not produce or tend to produce sludge on a significant scale.

Asphaltenes play an important role in controlling the viscous behavior of crude oil and the stability and compatibility during storage and transportation. This has been extensively revealed in the literature by rheological studies with crude oils from different sources. Although crude oils are generally considered Newtonian fluids, crude oils with high amount and more complex asphaltene molecules will exhibit pronounced pseudoplastic, non-Newtonian behavior.

Asphaltenes are believed to exist as micelles in petroleum. Resins, which can be considered as low-molecular-weight asphaltenes, are also known as maltenes and act as a solvent for the other constituents. Thus, heavy oil is generally considered to contain a disperse phase of asphaltenes complexed with high-molecular-weight components of the maltenes (resins) and liquid hydrocarbons in the form of a micelle. An equilibrium state exists under these conditions, and the micelles are considered to be peptized (i.e., colloidally dispersed). However, if the C/H ratio of the maltenes is lowered, the resins that are absorbed in the asphaltenes are partially desorbed. The consequence of this change is an alteration of the equilibrium, which results in the asphaltene particles not being completely surrounded by resins and they are mutually attracted. This ends up to precipitation of asphaltenes, which appear as sludge.

The most common methods to evaluate the stability/compatibility of crude oils and blends of crude oils can be classified as direct and indirect as follows (Speight, 2001):

1.3.5.1 Direct Test Methods

- *Spot-Test*. It gives a visual determination of oil stability and hence the results are slightly subjective.
- *Hot-Filtration Test*. It gives the total amount of sediment in the oil but does not give information about the stability of the oil.
- *Xylene Equivalent Test*. It determines the necessary proportion of xylene in a blend with isooctane to obtain a homogeneous spot on a chromatographic paper when blended with an equal quantity of the specified sample. The lower the proportion of xylene, the better the compatibility of the sample.
- *Bottle Test*. This test is gravimetric in nature and easy to perform and is the traditional standard method for crude oil–completion brine compatibility testing.
- *Gum Stability*. It is an approximate measure of the tendency to form gum during storage.
- *Water, Sediment, and Salt Contents*. The higher the bottom sediment and water content, the higher sludge and deposit formation rates that can be expected.

1.3.5.2 Indirect Test Methods

- *Ultimate or Elemental Analysis (C, H, O, N, S, Metals, and Ash Contents)*. The higher the nitrogen and sulfur contents in crude oils, the higher the sludge-formation tendencies.
- *Specific Gravity/API Gravity*. Crude oils having low API gravity (heavy oils) are more susceptible to sludge formation due to their higher content of polar/asphaltic constituents.
- *Viscosity*. The viscosity of the crude oil generally increases due to the presence of products of instability or compatibility processes.
- *Pour Point*. Crude oils with high pour point are more waxy and tend to form wax-like materials that enhance sludge formation.
- *Asphaltenes*. The higher the asphaltenes content, the greater the tendency of crude oils to form sludge, especially when blended with other noncompatible stocks.
- *Total Acidity (Acid Number)*. Crude oils of higher acidities may exhibit a tendency of instability.
- *Characterization Factor*. If the characterization factor is above 12 (paraffinic), the crude oil is expected to form waxy deposits.

1.3.5.3 Methods Based on SARA Analysis

- *Colloidal Instability Index (CII)*. This index expresses the stability of asphaltenes in terms of SARA (Saturates, Aromatics, Resins, Asphaltenes) fractions and is defined as the mass ratio between the sum of asphaltenes and unfavorable components of its stability in the oil, that is, its flocculants (Saturates) and the sum of peptizing agents (Aromatics and Resins), which are components favorable to the stability of asphaltenes present in a specific oil (Asomaning, 2003):

$$\mathrm{CII} = \frac{\text{Asphaltenes } (\%) + \text{Saturates } (\%)}{\text{Resins } (\%) + \text{Aromatics } (\%)} \tag{1.18}$$

CII can also be represented in a plot of (Resins+Aromatics) versus (Asphaltenes+Saturates). The lower the CII value, the greater the stability of asphaltenes in the oil. CII gives a relative way to assess whether the oil is more or less stable compared with others. If CII $\geq$ 0.9, asphaltenes are unstable in the oil. If CII $<$ 0.7, the asphaltenes are stable in the oil. For values between 0.7 and 0.9, there is uncertainty about the stability.

- *Stankiewicz Plot* (Stankiewicz et al., 2002). It uses a cross-plot of two ratios: (Saturates/Aromatics) versus (Asphaltenes/Resins). This type of plot gives a quick identification of asphaltene risk by separating the stable and unstable area.
- *Stability Cross-Plot* (*SCP*) (Sepulveda et al., 2010). It uses four plots to determine the stability of asphaltenes for any type of petroleum:
  1. (Resins/Asphaltenes)/(Saturates/Aromatics) versus (Aromatics/Asphaltenes)
  2. (Resins/Asphaltenes)/(Saturates/Aromatics) versus (Resins/Asphaltenes)
  3. (Saturates/Aromatics) versus (Resins/Asphaltenes)
  4. (Resins/Asphaltenes)/(Saturates/Aromatics) versus. (Aromatics/Saturates/Asphaltenes).

  Better confidence of the SCP method (92%) has been claimed compared with other methods (CII: 72%, Stankiewicz: 86%).

1.3.5.4 Other Methods

- *De Boer Plot* (de Boer et al., 1995). It uses a plot of *in situ* oil density versus undersaturation pressure. Higher risks are observed in case of light oil under high undersaturation pressure.
- *Heithaus Titration Method* (*P-value*). It gives the total amount of *n*-heptane that can be added before the oil becomes instable. The Heithaus titration is performed only with the toluene-soluble components of the oil. Three toluene solutions at different concentrations are titrated with a weak solvent such as isooctane. The weight of oil (W_a), the volume of toluene (V_s), and the volume of isooctane titrant (V_t) are recorded at the flocculation point, where asphaltenes just begin to precipitate for each solution. The flocculation ratio (FR) and dilution concentration (C) are calculated as follows (Heithaus, 1962):

$$\mathrm{FR} = \frac{V_s}{V_s + V_t} \tag{1.19}$$

$$C = \frac{W_a}{V_s + V_t} \tag{1.20}$$

A plot of FR versus C is made and the intercepts are determined ($\mathrm{FR}_{\max}$ and $C_{\min}$). The Heithaus parameters are defined as follows:

$$\text{Peptizability of asphaltenes:}\quad p_\mathrm{a} = 1 - \mathrm{FR}_{\max} \tag{1.21}$$

$$\text{Solvent power of maltenes:}\quad p_0 = \mathrm{FR}_{\max}(1/C_{\min} + 1) \tag{1.22}$$

$$\text{Overall compatibility of residuum:}\quad P = p_0/(1 - p_\mathrm{a}) = 1/C_{\min} + 1 \tag{1.23}$$

Larger values of p_a indicate peptizable asphaltenes and larger values of P indicate an overall compatible system. A larger p_o value is subject to a mixed interpretation. Oil with $P < 1$ is considered as instable oil.

- *Intrinsic Stability* (*S*-value). It describes a procedure for quantifying the intrinsic stability of the asphaltenes in an oil matrix, by using an optical device. Similarly to *P*-value method, three parameters are determined:
  - *S*: It defines the state of peptization of the asphaltenes in oil and characterizes the global stability of the sample. Oil with a low *S*-value is likely to undergo flocculation of asphaltenes. Oils with high *S*-values are likely to maintain asphaltenes in a peptized state and do not lead to asphaltene flocculation when blended.
  - *Sa*: It represents the solvency requirements of the peptized asphaltenes and characterizes the aromaticity of asphaltenes. In other words, it gives the ability of asphaltenes to remain in colloidal dispersion. The lower the *Sa* value, the higher the aromaticity.
  - *So*. It identifies the power of peptization of oil and characterizes the aromaticity of resins and their capability to maintain asphaltenes in solution. The higher the value of *So*, the higher the aromaticity.

1.4 ASSAY OF PETROLEUM

A crude oil assay is a compilation of laboratory (physical and chemical properties) and pilot plant (distillation and product fractionation) data that characterize a specific crude oil. Assay analyses of whole crude oils are carried out by combining atmospheric and vacuum distillation units, which when combined will provide a TBP (True Boiling Point) distillation. The values of the distillation ranges of the distilled fractions are usually defined depending on the refinery product classifications. The most common distillation ranges used in international assays of crude oils are as follows:

- Light straight-run naphtha (LSRN): IBP–71 °C
- Medium straight-run naphtha (MSRN): 71–177 °C
- Heavy straight-run naphtha (HSRN): 177–204°C
- Jet fuel (JF): 204–274 °C
- Kerosene (K): 274–316 °C

- Straight-run gasoil (SRGO): 316–343 °C
- Light vacuum gasoil (LVGO): 343–454 °C
- Heavy vacuum gasoil (HVGO): 454–538 °C
- Vacuum residue (VR): 538 °C+

Sometimes, the atmospheric residue (343 °C+, blend of LVGO, HVGO and vacuum residue) is also obtained and characterized. A detailed hydrocarbon analysis of crude oil off-gas is also run.

The most common applications of petroleum assays in different areas in petroleum refining industry are as follows:

- To provide extensive detailed experimental data for refiners to establish the compatibility of a crude oil for a particular petroleum refinery
- To anticipate if the crude oil will fulfill with the required product yield, quality, and production
- To determine if during refining the crude oil will meet with environmental and other issues
- To help refiners make decisions about changes in plant operation, development of product schedules, optimize the refining process, and examination of future processing ventures
- To supply engineering companies with detailed crude oil analyses for preparing the process design of petroleum refining plants and detailed refinery engineering
- To facilitate the companies' crude oil pricing and to negotiate possible penalties due to impurity content and other undesired properties.

An assay varies in depth and complexity depending on the crude oil type and its end use. The assay can be an inspection assay or comprehensive assay. There are various types of assays that vary considerably in the amount of determined experimental information:

- Assays that include yields and properties of those streams used as feed for catalytic reforming (naphtha) and catalytic cracking (gas oils)
- Assays that give more details for potential production of lubricant oil and/or asphalt
- Assays that include minimal information such as a distillation curve (typically TBP distillation, true boiling point) for the crude and a specific gravity curve
- Assays that are complete and include experimental characterization of the whole crude oil and of various boiling range fractions, curves of TBP, specific gravity, and sulfur content.

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