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History and Terminology

1.1 Introduction

Crude oil (also commonly referred to as “petroleum”) is typically a mixture of hydrocarbon derivatives that occurs widely in the sedimentary rocks in the form of gases, liquids, semisolids, or solids. Crude oil provides not only raw materials for the ubiquitous plastics and other products but also fuel for energy, industry, heating, and transportation. Chemically, crude oil is an extremely complex mixture of organic compounds many of which (in conventional crude oil) are hydrocarbon derivatives along with minor amounts of nitrogen-containing compounds, oxygen-containing compounds, and sulfur-containing compounds as well as trace amounts of metal-containing compounds (Chapter 2) (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017).

However, over the past several decades, the feedstocks available to refineries have generally decreased in API gravity and a major focus in refineries is to develop processing options for the viscous feedstocks (Khan and Patmore, 1997; Gary et al., 2007; Rana et al., 2007; Rispoli et al., 2009; Stratiev and Petkov, 2009; Stratiev et al., 2009; Motaghi et al., 2010a, 2010b; Speight, 2011a; Hsu and Robinson, 2017; Speight, 2017). Simultaneously, the changing crude oil properties are reflected in changes such as an increase in asphaltene constituents, and an increase in sulfur, metal, and nitrogen contents. Pretreatment processes for removing such constituents or at least negating their effect in thermal process would also play an important role.

The limitations of processing these heavy feedstocks depend to a large extent on the amount of higher molecular weight constituents (i.e., asphaltene constituents and resin constituents) that contain the majority of the heteroatom-containing compounds, which are responsible for high yields of thermal and catalytic coke. Be that as it may, the essential step required of a modern refinery is the upgrading

of heavy feedstocks, particularly the complex atmospheric residua and vacuum residua.

Upgrading feedstocks such as heavy oils and residua began with the introduction of hydrodesulfurization processes (Speight, 2000). In the early days, the goal was desulfurization but, in later years, the processes were adapted to a 10–30% partial conversion operation, as intended to achieve desulfurization and obtain low-boiling fractions simultaneously, by increasing severity in operating conditions. However, as refineries have evolved and feedstocks have changed, refining viscous feedstocks has become a major part of modern refinery practice and there has also been the evolution and the necessity of the development of process configurations to accommodate the viscous feedstocks (Khan and Patmore, 1997; Parkash, 2003; Gary et al., 2007; Speight, 2011a; Hsu and Robinson, 2017; Speight, 2017).

For example, hydrodesulfurization of the light (low-boiling) distillate (naphtha or kerosene) is one of the more common catalytic hydrodesulfurization processes since it is usually used as a pretreatment of such feedstocks prior to deep hydrodesulfurization or prior to catalytic reforming. A similar concept of pretreating residua prior to hydrocracking to improve the quality of the products is also practiced (Speight, 2011a). Hydrodesulfurization of such feedstocks is required because sulfur compounds poisoning the precious-metal catalysts used in the hydrocracking process can be achieved under relatively mild conditions. If the feedstock arises from a cracking operation (such as cracked residua), hydro-pretreatment will be accompanied by some degree of saturation resulting in increased hydrogen consumption.

In fact, since the so-called oil shocks of the 1970s, the refining industry has been the subject of the forces which have hastened the development of refineries such as (1) the demand for products such as gasoline, diesel, fuel oil, and jet fuel; (2) feedstock supply, specifically the changing quality of crude oil and geopolitics between different countries; (3) the emergence of alternate feed supplies such as heavy crude oil, extra heavy crude oil, and tar sand—collectively known as viscous feedstocks; (4) technology development such as new catalysts and processes, especially processes involving the use of hydrogen; and (5) environmental regulations that include more stringent regulations in relation to sulfur in gasoline and diesel (Parkash, 2003; Gary et al., 2007; Speight, 2011a; Hsu and Robinson, 2017; Speight, 2017).

The viscous feedstocks by virtue of the generation and maturation process that contribute to the formation of these feedstocks have lesser amounts of hydrocarbon derivatives and have properties characteristics that affect their flowability in the processes of recovery, pipeline transportation, and in the refinery. Moreover, the key to feedstock refining is, as in any industrial process, knowledge of the character of the feedstock. Chemical composition is the starting point for the oil

characterization and it has a major impact on other properties, including key properties for their dynamics, such as density and viscosity (Chapter 2).

The particular characteristics of the viscous oils are mainly attributed to a biodegradation process in which microorganisms on a geological time scale degrade light and medium hydrocarbons, making the reserves rich in polynuclear aromatic derivatives, resin constituents, and asphaltene constituents (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). Microbial degradation reaches optimal temperatures below 80 °C (715 °F), promoting oil oxidation, reduction of the gas/oil ratio (GOR), and increasing density, acidity, and viscosity as well as the relative proportion of sulfur and heavy metals. In addition to bio-processes, the formation of heavy crude oil (as well as extra heavy crude oil and tar sand bitumen) occurs through mechanisms such as water washing and phase fractionation, which are based on the loss of a significant fraction of the original source mass as well as removal of lower boiling constituents (and fractions) by physical rather than bio-processes.

The viscous feedstocks display a high content of high molecular weight constituents that contain elevated levels of heteroatom constituents including sulfur, nitrogen, oxygen, and metals that require modification of the refinery processing options (Speight, 2011a, 2017). Typically, the molecules present in the viscous oils have more than 15 carbon atoms in the chain which can lead to the generation of products (in the refinery) such as a low yield of content of high-octane naphtha and kerosene. Although the amount of compounds containing heteroatom constituents is relatively small, the effect of these compounds on the refining processes and the properties of the products are usually significant.

Chemical species containing sulfur atoms are often regarded as harmful for their effects on the refining process. The most common types are thiol derivatives (RSH), sulfide derivatives (R^1SR^2 , where R^1 and R^2 are the same or different organic moieties), and thiophene and derivatives.

By way of definition, thiophene (C_4H_4S) is a heterocyclic compound (the sulfur is in a ring structure) that is a colorless liquid with a benzene-like odor that is only one of several sulfur-containing derivatives that occur in crude oil and the viscous oils (Figure 1.1).

These derivatives consist of thiol mercaptan derivatives (RSH, where R is an alkyl moiety or an aromatic moiety), sulfide derivatives (R^1SR^2 , where R^1 and R^2 are the same or different moieties), disulfide derivatives (R^1SSR^2 , where R^1 and R^2 are the same or different moieties), and cyclic sulfide derivatives where the sulfur atom occurs in a six-membered saturated ring system consisting of five carbon atoms and one sulfur atom. There are also examples where the sulfur atom occurs in a

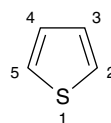


Figure 1.1 Thiophene (the numbers, 2–5, indicate the positions of the substitutable hydrogen atoms).

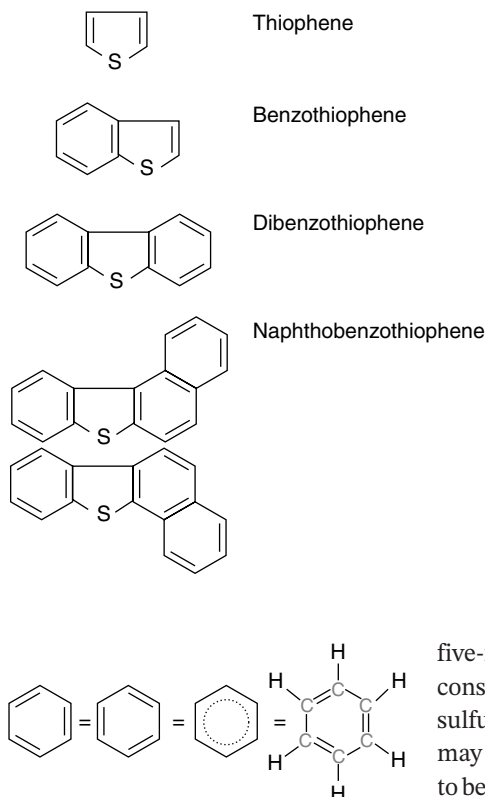


Figure 1.3 Benzene (showing the various alternate structures; in terms of reactivity, the structures are equivalent).

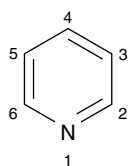


Figure 1.4 Pyridine (the numbers, 2–6, indicate the positions of the substitutable hydrogen atoms).

Figure 1.2 Examples of organic sulfur derivative that occur in crude oil and the viscous oils.

five-membered saturated ring system consisting of four carbon atoms and one sulfur atom. The remaining derivatives may be (arbitrarily or simple) considered to be derivatives of thiophene (Figure 1.2).

Thiophene is a planar five-membered ring and reacts very much in the manner of benzene derivatives.

Benzene is an organic hydrocarbon (C_6H_6), that is, the benzene molecule is composed of six carbon atoms joined in a planar ring with one hydrogen atom attached to each carbon (Figure 1.3).

The nitrogen compounds are generally basic, formed by pyridine and its homologs (Figure 1.4). Pyridine is a basic heterocyclic organic compound (C_5H_5N) which is structurally related to benzene, with one methine ($-C-H$) group replaced by a nitrogen atom. It is a weakly alkaline, water-miscible liquid.

However, nitrogen compounds can also occur in nonbasic forms, formed by species including pyrrole derivatives, indole derivatives, and carbazole derivatives (Figure 1.5) (Speight, 2014a, 2017). Significant amounts of porphyrin derivatives (which contain nickel, Ni, and vanadium, V) may occur in the nonbasic fraction of the nitrogen compounds. Other

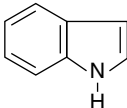
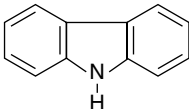
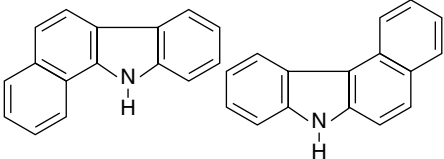
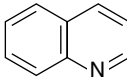
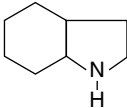
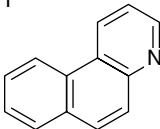
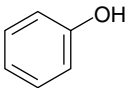
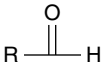
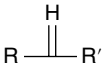
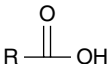
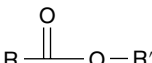
Nonbasic		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Benzo(a)carbazole	$C_{16}H_{11}N$	
Basic		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Benzo(f)quinoline	$C_{13}H_9N$	

Figure 1.5 Examples of organic nitrogen derivatives that occur in crude oil and the viscous oils.

metal-containing derivatives are generally present in the form of organic salts ($R-M^+$) where R is an organic moiety and M is a metal dissolved in oil-emulsified water. Heavy crude oils often contain a large portion of nickel and vanadium, which form chelates with porphyrins that are responsible for catalyst contamination and corrosion problems (Speight, 2014c).

Oxygenated compounds appear as carboxylic derivatives (RCO_2H , where R is an aliphatic group or aromatic group) and phenol derivatives (ArCO_2H , where Ar is an aromatic group), although the presence of ketone derivatives (R^1COR^2 , where R^1 and R^2 are either aliphatic or aromatic hydrocarbon groups) and ether derivatives (R^1OR^2 , where R^1 and R^2 are either aliphatic or aromatic hydrocarbon groups) have also been identified in some feedstocks (Figure 1.6) (Speight, 2014a, 2017). The content of the oxygen-containing compounds (especially the carboxylic acid derivatives) and the phenol derivatives determines the acidity of the feedstock and, hence, the corrosivity (Speight, 2014c), which is particularly important in the refining processes. These features can occur on the same molecular structure, further increasing the complexity and difficulty of the characterization of the compounds present in the crude oil.

Due to the impossibility of an elemental characterization of crude oils and viscous oils because of their complex nature, a complete characterization has been satisfactorily obtained by fractionation, based on fraction polarity and solubility (Chapter 3). The saturates, aromatics, resins, asphaltene (SARA) analysis is the most widely used method to subdivide refinery feedstocks (and many higher boiling refinery products) into four subfractions, namely (1) a saturates fraction, (2) an aromatics fraction, (3) a resins fraction, and (4) an asphaltene fraction. The method produces the fractions based on molecular weight (by solvent treatment of the

Name	Functional group	Figure 1.6 Examples of organic oxygen derivatives that occur in crude oil and the viscous oils.
Alcohols	$\text{R}-\text{OH}$	
Phenols		
Ethers	$\text{R}-\text{O}-\text{R}'$	
Aldehydes		
Ketones		
Carboxylic acids		
Esters		

feedstock) and polarity through a chromatographic technique. Thus, by using different solvents (such as *n*-pentane or *n*-heptane), the asphaltene fraction can be separated from the whole feedstock (or a topped feedstock—the feedstock from which the more volatile constituents boiling up to, say, 200 °C, 390 °F have been removed)—while an adsorbent is (or different adsorbents are) employed to separate the saturates, aromatics, and resin fractions (Chapter 3) (Speight, 2014a, 2015a). The method is reproducible and applicable to a wide variety of heavy crude oil, extra heavy crude oil, tar sand bitumen, and crude oil residua.

Finally, there is not one single heavy feedstock upgrading solution that will fit all refineries. Market conditions, existing refinery configuration, and available crude prices all can have a significant effect on the final configuration. Furthermore, a proper evaluation, however, is not a simple undertaking for an existing refinery. The evaluation starts with an accurate understanding of the market for the various products along with corresponding product values at various levels of supply. The next step is to select a set of crude oils that adequately cover the range of crude oils that may be expected to be processed. It is also important to consider new unit capital costs as well as incremental capital costs for revamp opportunities along with the incremental utility, support, and infrastructure costs. The costs, although estimated at the start, can be better assessed once the options have been defined leading to the development of the optimal configuration for refining the incoming feedstocks.

In fact, the limitations of processing these heavy feedstocks depend to a large extent on the amount of higher molecular weight constituents (i.e., asphaltene constituents and resin constituents) that contain the majority of the heteroatom-containing compounds, which are responsible for high yields of thermal and catalytic coke (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). Be that as it may, the essential step required of a modern refinery is the knowledgeable upgrading of the heavy feedstocks through the data acquisition programs (analytical test methods) that provide indication of the behavior of the feedstocks during refining.

Furthermore, there is not one single upgrading option that will accommodate all of the viscous feedstocks and that will fit all refineries and feedstock composition can have a significant effect on the necessary processing configuration. Thus, a proper evaluation that starts with an analytical program that will identify the characteristics of the feedstocks accepted by the refinery as well as afford the luxury of predictability of the behavior of the feedstock constituents during refining.

Thus, the focus of this text is on the test methods that will assist the refiner to identify the appropriate options for the various viscous refinery feedstocks that are currently accepted as feedstocks for refineries. This chapter begins with a presentation of the terminology of the feedstocks.

1.2 Historical Perspectives

The history of any subject is the means by which the subject is studied in the hopes that much can be learned from the events of the past. In the current context, the occurrence and use of crude oil, crude oil derivatives (naphtha), and the viscous feedstocks (such as heavy crude oil, extra heavy crude oil, and tar sand bitumen) are not new. The use of crude oil and the viscous materials that seeped from outcrops was practiced in pre-Christian times and is known largely through historical use in many of the older civilizations, particularly the civilization of the Middle Eastern countries where seepages from outcrops were widely recognized (Henry, 1873; Abraham, 1945; Forbes, 1958a, 1958b; James and Thorpe, 1994; Speight, 2014a).

As a brief introduction to the historical aspects of the subject, crude oil (also known as petroleum) was originally referred to as “rock oil” which was derived from the Latin “petra” which, in turn, was derived from the Greek word “πέτρα” (meaning “rock” or “stone”) and “oleum” which originally meant “olive oil” and, in turn, was derived from the ancient Greek word “ἐλαιον” (élaion also meaning “olive oil”). However, the development of a system of terminology is more complex and has evolved from pre-Christian times (years typically designated by the term “BC”) to the present time and, with the incursion of the viscous feedstocks into refining processing, is continuing to evolve.

1.2.1 Pre-Christian Era Use of Heavy Oil and Bitumen

The word asphalt is derived from the Akkadian term “asphaltu” or “sphallo,” meaning to split, which is indicative of the early use of an asphalt as a mastic between stones.

As an explanatory note, the Akkadian Empire was the first ancient empire of Mesopotamia that existed after the long-lived southern Mesopotamian civilization of Sumer. The empire was centered in the city of Akkad and the immediately surrounding region, and the empire united the Sumerian and Akkadian speakers under one rule and language. Sargon of Akkad (also known as Sargon the Great and sometimes identified as the first person in recorded history to rule over an empire rather than a city-state) was the first ruler of the Akkadian Empire, known for his conquests of the Sumerian city-states in the 24th to 23rd centuries BC.

The term “asphaltu” was later adopted by the Homeric Greeks in the form of the signifying firm, stable, secure, and the corresponding verb ασφαλίζω ἴσω meaning to make firm or stable, to secure. On the other hand, the origin of the word bitumen is more difficult to trace and subject to considerable speculation. The word has been proposed to have originated in the Sanskrit, in which language the words

“jatu”, meaning pitch, and “jatukrit” occur and have been proposed to mean “pitch creating” (Speight, 2011b, 2014a, 2016).

From the Sanskrit, the word “jatu” was incorporated into the Latin language as “gwitu” and is reputed to have eventually morphed into the word “gwitumen” (supposedly meaning “pertaining to pitch”). Another word, “pixtumen” (which has been proposed and assumed to mean “exuding pitch” or “bubbling pitch”) is also reputed to have been in the Latin language, although the construction of this Latin word, from which the word “bitumen” was reputedly formed and derived, is certainly suspect (Speight, 2014a, 2016). However, there is the possibility that subsequent derivation of the word led to a shortened version (which eventually became the modern version) “bitûmen” from which the word has passed into the English language by way of the French language.

In this text for convenience and to avoid confusion that can exist from the use of different names, the word “bitumen” is used to indicate the naturally occurring viscous organic material that occurs in various deposits and outcrops. In the modern world, the word “asphalt” is used to indicate the manufactured organic material and does not include the inorganic aggregate that is mixed with the paving as a lay-down for road paving systems (Speight, 2014a, 2016).

More generally, bitumen (often incorrectly referred to as natural asphalt since the word “asphalt” is used to describe a refinery product) was used as mortar from very early times, and sand, gravel, or clay was employed in preparing these mastics. Bitumen-coated tree trunks were often used to reinforce wall corners and joints, for instance in the temple tower of Ninmach in Babylon. In vaults or arches, a mastic-loam composite was used as mortar for the bricks, and the keystone was usually dipped in bitumen before being set in place. The use of bituminous mortar was introduced into the city of Babylon by King Hammurabi, but the use of bituminous mortar was abandoned toward the end of the reign of King Nebuchadnezzar in favor of lime mortar to which varying amounts of bitumen were added. The Assyrians recommended the use of bitumen for medicinal purposes, as well as for building purposes, and perhaps there is some merit in the fact that the Assyrian moral code recommended that bitumen, in the molten state, be poured onto the heads of criminals as a form of punishment.

One of the earliest recorded uses of bitumen was by the pre-Babylonian inhabitants of the Euphrates Valley in southeastern Mesopotamia, present-day Iraq, formerly called Sumer and Akkad and, later, Babylonia. In this region, there are various bitumen deposits, and uses of the material have become evident. For example, King Sargon Akkad (Agade) (at about 2550 BC) was (for reasons that are lost in the annals of time) set adrift by his mother in a basket of bulrushes on the waters of the Euphrates and he was discovered by Akki the husbandman (the irrigator), whom he brought up to serve as gardener in the palace of Kish. Sargon eventually ascended to throne.

On the other hand, the bust of Manishtusu, King of Kish, an early Sumerian ruler (about 2270 BC), was found in the course of excavations at Susa in Persia, and the eyes, composed of white limestone, are held in their sockets with the aid of bitumen. Fragments of a ring composed of bitumen have been unearthed above the flood layer of the Euphrates at the site of the prehistoric city of Ur in southern Babylonia, ascribed to the Sumerians of about 3500 BC.

The Tigris-Euphrates valley, in what is now Iraq, was inhabited as early as 4000 BC by the people known as the Sumerians who established one of the first great cultures of the civilized world. The Sumerians devised the cuneiform script, built the temple-towers known as ziggurats, and had an impressive law, literature, and mythology. As the culture developed, bitumen was used as a sealant (sometimes incorrectly referred to as natural occurring bitumen). In fact, there is evidence that bitumen was used as a sealant for water channels to, and within, several of the ancient cities in the region (Speight, 1978).

Nevertheless, these writings do offer documented examples of the use of crude oil and related materials. For example, in the Epic of Gilgamesh written more than 2,500 years ago, in anticipation of a forthcoming deluge, the principal of the story builds an ark (a very large boat) to accommodate and save his family as well as a host of animals. The wooden boat is caulked with bitumen and pitch (see for example, Kovacs, 1990) and in a related story, also set in Mesopotamia just prior to the deluge (the Biblical Flood), (it is not the intent here to discuss the similarities or relationship or origin of the two stories), a man (Noah) is commanded to build a boat that also includes instructions for caulking the vessel with pitch (Genesis 6:14).

Make yourself an ark of cypress wood; rooms shalt thou make in the ark, and shalt coat it with pitch inside and out.

The occurrence of slime (bitumen) pits in the Valley of Siddim, a valley at the southern end of the Dead Sea, is also noted (Genesis 14:10). There is also reference to the use of tar as a mortar when the Tower of Babel was under construction (Genesis 11:3).

And they said one to another, Go to, let us make brick, and burn them thoroughly. And they had brick for stone, and slime had they for mortar.

In the Septuagint, or Greek version of the Bible, this work is translated as “asphaltos” and in the Vulgate or Latin version, as bitumen. In the Bishop’s Bible of 1568 and in subsequent translations into English, the word is given as slime. In the Douay translation of 1600, it is “bitume” while in the German version of the Bible (assigned to Martin Luther), it appears as the word “thon”—the word is of

linguistically questionable origin and has been suggested to mean “clay.” Another example of the use of pitch (and slime) is given in the story of Moses (Exodus 2:3):

And when she could no longer hide him, she took for him an ark of bulrushes, and daubed it with slime and with pitch, and put the child therein; and she laid it in the flags by the river’s brink.

It is convenient (if not very reasonable) to assume that the word “slime” referred to a lower melting bitumen (such as extra heavy crude oil) whereas the word “pitch” referred to a higher melting material—the slime acting as a flux for the pitch.

It is most probable that, in both these cases, the *pitch* and the *slime* were obtained from the seepage of oil to the surface, which was a fairly common occurrence in the area. And during biblical times, bitumen was exported from Canaan to various parts of the countries that surround the Mediterranean (Armstrong, 1997).

In terms of liquid products, there is a noteworthy reference that relates to bringing oil out of flinty rock (Deuteronomy 32:13). The exact nature of the oil is not described nor is the nature of the rock. The use of oil for lamps is also referenced (Matthew 23:3) but whether it was mineral oil (a crude oil derivative such as naphtha or kerosene) or whether it was vegetable oil is not known.

Excavations conducted at Mohenjo-Daro and Harappa (founded and occupied in approximately 2500 BC) in the Indus Valley indicated that a bitumen-type mastic composed of a mixture of bitumen, clay, gypsum, and organic matter was found between two brick walls in a layer about 25 mm thick, probably a waterproofing material. Also unearthed was a bathing pool that contained a layer of mastic on the outside of its walls and beneath its floor.

Also in the Bronze Age (approximately 3300 to 1200 BC), dwellings were constructed on piles in lakes close to the shore to better protect the inhabitants from the ravages of wild animals and attacks from marauders. The wooden piles were preserved from decay by coating with bitumen and there are also references to deposits of bitumen at Hit (the ancient town of Tuttul on the Euphrates River in Mesopotamia) and the bitumen from these deposits was transported to Babylon for use in construction (Herodotus, *The Histories*, Book I). There is also reference (Herodotus, *The Histories*, Book IV) to a Carthaginian story in which birds’ feathers smeared with pitch are used to recover gold dust from the waters of a lake.

Use of bitumen by the Babylonians (1500 to 538 BC) is also documented and each monarch commemorated their reign and perpetuated their name by construction of building or other monuments. This includes references to deposits of bitumen at Hit (the ancient town of Tuttul on the Euphrates River) and the bitumen from these deposits was transported to Babylon for use in construction (Herodotus, *The Histories*, Book I). There is also reference (Herodotus, *The Histories*, Book IV) to a Carthaginian story in which birds’ feathers smeared with pitch are used to recover

gold dust from the waters of a lake. Also, the use of bitumen mastic as a sealant for water pipes, water cisterns, and in outflow pipes leading from flush toilets in ancient cities such as Babylon, Nineveh, Calah, and Ur has been observed and the bitumen lines are still evident in uncovered systems (Speight, 1978).

Early references to crude oil and its derivatives occur in the Bible, although by the time the various books of the Bible were written, the use of crude oil and bitumen was established. For example, the combustion properties of bitumen (and its fractions) were known in Biblical times. There is the reference to these properties (Isaiah 34:9) when it is stated that:

And the stream thereof shall be turned into pitch, and the dust thereof into brimstone, and the land thereof shall become burning pitch. And the streams thereof shall be turned into pitch.

It shall not be quenched night nor day; the smoke thereof shall go up forever: from generation to generation it shall lie waste; none shall pass through it.

It can be concluded (based on current knowledge) that the effects of the burning bitumen and sulfur (brimstone) were long lasting and quite devastating.

The Egyptians were the first to adopt the practice of embalming their dead rulers and wrapping the bodies in cloth. Before 1000 BC, bitumen was rarely used in mummification, except to coat the cloth wrappings and thereby protect the body from the elements. From 500 to about 40 BC, bitumen was generally used both to fill the corpse cavities (after the viscera had been removed) as well as to coat the cloth wrappings. The word *mûmûia* first made its appearance in Arabian and Byzantine literature about 1000 AD, signifying bitumen. In fact, it was through the spread of the Islamic Empire that, it is believed, brought Arabic science and the use of bitumen to Western Europe.

In the Roman world, bitumen was also an important commodity and could also be used for medicinal purposes such as to stop bleeding, heal wounds, drive away snakes, treat cataracts, and straighten out eyelashes which inconvenience the eyes as well as a wide variety of other diseases.

From the same roots as used by the pre-Christian builders, the Anglo Saxon word “cwidu” (mastic, adhesive) was derived. Also, the German word “kitt” (translated as filler, cement, or mastic) which is also found in the old Norse language as being descriptive of the material used to waterproof the long ships and other sea-going vessels. It is just as (perhaps even more than) likely that the word is derived from the Celtic *bethe* or *beithe* or “bedw” that was the birch tree that was used as a source of resin (tar). From this, the word appears in Middle English as *bithumen* (Speight, 2014a, 2016).

In fact, a variety of words exist in ancient languages which, from the use of the words in the relevant contexts, can be proposed as referring to bitumen

Table 1.1 Examples of the Origins of Words Related to Crude Oil and Bitumen

Language	Word	Possible meaning
Sumerian	esir	Petroleum, bitumen
	esir-harsag	Rock asphalt
	esir-ud-du-a	Pitch
	kupru	Slime
	kupru	Pitch
Sanskrit	jatu	Bitumen
	Jatu	Pitch
	śilā-jatu	Rock asphalt
Assyrian/Akkadian	idd	Bitumen
	Ittû	Bitumen
	it-tû-u	Bitumen
	amaru	Bitumen
	sippatu	Pitch
Greek	maltha	Soft asphalt
	asphaltos	Bitumen
	pittasphaltos	Rock asphalt
	pittolium	Rock oil
	pittolium	Rock asphalt
	pissa	Pitch
	pitta	Pitch
Latin	maltha	Soft asphalt
	bitumen liquidum	Soft asphalt
	pix	Pitch

(Table 1.1) (Abraham, 1945). From the Greek language, the word passed into (early medieval) Latin as “asphaltum” or “aspaltum” and from there into French (“asphalte”) and Old English (“aspaltoun”).

In addition to bitumen, there was also an interest in the distillation product derived from crude oil (nafta, which is presumably the product now referred to as naphtha) which was also derived from the thermal treatment of bitumen. It was discovered that this material could be used as an illuminant and as a supplement to asphalt incendiaries in warfare. For example, there are records of the use of mixtures of pitch and/or naphtha with sulfur as a weapon of war during the Battle of Palatea, Greece, in the year 429 BC (Forbes, 1959).

1.2.2 Post-Christian Era Use of Heavy Oil and Bitumen

Approximately two thousand years ago, Arabian scientists developed methods for the distillation of crude oil, which were introduced into Europe by way of Spain. This represents another documented use of the volatile derivatives of crude oil which led to a continued interest in crude oil and its derivatives as medicinal materials and materials for warfare, in addition to the usual construction materials.

There are references to the use of naft as an incendiary material (Greek fire, a precursor and chemical cousin to napalm) during various battles (James and Thorpe, 1994). Greek fire is also recorded as being used in the period 674–678 AD when the city of Constantinople was saved by the use of the fire against the by an Arab fleet (Davies, 1996). In 717–718 AD, Greek fire was again used to save the city of Constantinople from attack by another Arab fleet; again with deadly effect (Dahmus, 1995).

Many other references to bitumen occur throughout the empires of Greece and Rome and from then to the Middle Ages, early scientists (alchemists) frequently alluded to the use of bitumen for a variety of purposes of which bitumen use as a mastic appears to have been popular. In later times, both Christopher Columbus and Sir Walter Raleigh (depending upon the country of origin of the biographer) have been credited with the discovery of the bitumen deposit on the island of Trinidad and apparently used the material to caulk the ships.

Bitumen (or a bitumen-type material, i.e., a viscous naturally occurring material) was used in prescriptions, as early as the 12th Century, by the Arabian physician Al Magor, for the treatment of contusions and wounds. The 13th Century scientist Al-Kazwîni alluded to the healing properties of mûmûia, and Ibn Al-Baitâr gives an account of its source and composition. The region around Baku (currently, the capital and largest city of Azerbaijan, as well as the largest city on the Caspian Sea and of the Caucasus region) was also reported (by Marco Polo in 1271–1273) as having an established commercial crude oil industry. It is believed that the prime interest was in the kerosene fraction that was then known for its use as an illuminant. By inference, it has to be concluded that the distillation, and perhaps the thermal decomposition, of crude oil were established technologies. If not, Polo's diaries might well have contained a description of the stills or the reactors.

In addition, bitumen was investigated in Europe during the Middle Ages (Bauer, 1546, 1556), and the separation and properties of bituminous products were thoroughly described. Other investigations continued, leading to a good understanding of the sources and use of this material even before the birth of the modern crude oil industry (Forbes, 1958a, 1958b). Also, in Europe, Engelbert Kämpfer (1651–1716) gave a detailed account of the collection of bitumen in his treatise *Amoenitates Exoticae* (Exotic Pleasantries) as well as the different grades and types and the use of the material as a curative in medicine.

There are also records of the use of crude oil spirit, probably a higher boiling fraction of or than naphtha that closely resembled the modern-day liquid paraffin, for medicinal purposes. In fact, the so-called liquid paraffin has continued to be prescribed up to modern times. The naphtha of that time was obtained from shallow wells or by the destructive distillation of asphalt.

Parenthetically, the destructive distillation operation may be likened to modern thermal cracking or coking operations (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017) in which the overall objective is to convert the feedstock into distillates for use as fuels. This particular interest in crude oil and its derivatives continued with an increasing interest in nafta (naphtha) because of its aforementioned use as an illuminant and as a supplement to asphaltic incendiaries for use in warfare.

In summary, the use of crude oil and bitumen has been observed for almost 6000 years (Mallowan and Rose, 1935; Nellensteyn and Brand, 1936; Mallowan, 1954; Marschner et al., 1978). During this time, the use of the raw materials and the products has progressed from the relatively simple use of asphalt from Mesopotamian seepage sites to the present-day refining operations that yield a wide variety of products and petrochemicals (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017, 2019a).

1.3 Definitions and Terminology

While the focus of this chapter is predominantly on the various viscous refinery feedstocks, the nonviscous fractions of crude oil are also used for the production of products through the application of thermal cracking processes and catalytic cracking processes. These are (1) crude oil and (2) other assorted crude oils such as opportunity crude oil, high-acid crude oil, and foamy oil.

These feedstocks are produced from reservoirs and are part of the crude oil family but are, nevertheless, worthy of mention as potential feedstocks for comparison with the viscous feedstocks which, when submitted to thermal cracking processes and catalytic cracking processes, lead to a range of products that also includes petrochemical products (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017, 2019a, 2021).

Throughout the millennia in which crude oil has been known and used, it is only in the last decade or so that some attempts have been made to standardize the nomenclature and terminology. But confusion may still exist. Therefore, it is the purpose of this chapter to provide some semblance of order into the disordered state that exists in the segment of crude oil technology that is known as terminology.

Terminology is the means by which various subjects are named so that reference can be made in conversations and in writings and so that the meaning is passed on.

Definitions are the means by which scientists and engineers communicate the nature of a material to each other and to the world, through either the spoken or the written word. Thus, the definition of a material can be extremely important and have a profound influence on how the technical community and the public perceive that material.

Because of the need for a thorough understanding of crude oil and the associated viscous feedstocks, it is essential that the definitions and the terminology of crude oil science and technology be given prime consideration (Meyer and De Witt, 1990). This will aid in a better understanding of crude oil, its constituents, and its various fractions. Of the many forms of terminology that have been used, not all have survived, but the more commonly used are illustrated here. Particularly troublesome, and more confusing, are those terms that are applied to the more viscous materials, for example the use of the terms bitumen and asphalt (Speight, 2014a, 2016). This part of the text attempts to alleviate much of the confusion that exists, but it must be remembered that the terminology of crude oil is still open to personal choice and historical usage.

In general, the definition of crude oil has been varied, unsystematic, diverse, and often archaic (Speight, 2014a, 2017, 2021) because the terminology used to describe crude oil is subject to many conventions of which major ones are chemistry-aligned definitions, company-aligned definitions, engineering-aligned definitions, and definitions aligned with the geological sciences. Thus, the long-established use of an expression, however inadequate it may be, is altered with difficulty, and a new term, however precise, is at best adopted only slowly.

Of the many forms of terminology that have been used not all have survived and the more commonly used are illustrated here but, as a note, particularly troublesome, and more confusing, are those terms that are applied to the more viscous materials, for example the use of the terms bitumen and asphalt. This part of the text attempts to alleviate much of the confusion that exists, but it must be remembered that the terminology of crude oil is still open to personal choice and historical usage.

By way of introduction, when crude oil occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark to light colored liquid, it is often referred to as conventional crude oil. Heavy crude oils are categorized as types of crude oil that are different from conventional crude oil insofar as they are much more difficult to recover (but can be recovered) from the subsurface reservoir (Speight, 2014a). There have been arbitrary attempts to rationalize the definition of heavy crude oil (and other naturally occurring viscous materials such as extra heavy crude oil and tar sand bitumen) based upon viscosity, API gravity, and density when it is preferable to use a more practical method

(that is less prone to misinterpretation and confusion) such as the method of recovery of the material (Speight, 2014a, 2017, 2021).

Viscous feedstocks are refinery feedstocks such as crude oil residua, (1) heavy crude oil, (2) extra heavy crude oil, (3) tar sand bitumen, and (4) distillation residua that have a low volatility, high density, and high viscosity. Although other feedstocks such as naphtha, kerosene, and gas oil are also used as feedstocks for thermal processes and catalytic processes in the refinery (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017), the focus of this book remains on the viscous feedstocks.

1.3.1 Nonviscous Feedstocks

By way of introduction, when crude oil occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark to light colored liquid, it is often referred to as conventional crude oil. A heavy crude oil is categorized as a type of crude oil that is different from conventional crude oil insofar as the heavy crude oil is typically recovered using a thermal-based (i.e., a steam-based) process and is much more difficult to recover from the subsurface reservoir (Speight, 2014a).

In spite of the different recovery methods that are applied to heavy oil, the definition of heavy crude oil is often arbitrarily (and incorrectly) based on the API gravity or viscosity, although there have been arbitrary attempts to rationalize the definition based upon viscosity, API gravity, and density when it is preferable to use the method of recovery of the material (Speight, 2014a, 2017, 2021).

1.3.1.1 Crude Oil

The definition of crude oil has been varied, unsystematic, diverse, and often archaic. Furthermore, the terminology of crude oil is a product of many years of growth. Thus, the long-established use of an expression, however inadequate it may be, is altered with difficulty, and a new term, however precise, is at best adopted only slowly.

Crude oil is a naturally occurring mixture of hydrocarbons, generally in a liquid state, which may also include compounds of sulfur nitrogen oxygen metals and other elements (ASTM D4175, 2021). Crude oil has also been defined (ITAA, 1936) as: (1) any naturally occurring hydrocarbon, whether in a liquid, gaseous, or solid state; (2) any naturally occurring mixture of hydrocarbons, whether in a liquid, gaseous, or solid state; and (3) any naturally occurring mixture of one or more hydrocarbons, whether in a liquid, gaseous, or solid state and one or more of the following, that is to say, hydrogen sulfide, helium, and carbon dioxide. The definition also includes any crude oil as defined by section (1), (2), or (3) that has been returned to a natural reservoir.

Table 1.2 Boiling Fractions of Conventional Crude Oil

Fraction	Boiling range	
	°C	°F ^a
Low boiling range naphtha	30–100	30–210
Medium boiling range naphtha	100–150	210–300
High boiling range naphtha	150–180	300–400
Fuel oil (six classes)	175–600	345–1,110
Middle distillates ^b	180–290	400–555
Kerosene	180–260	355–500
Light gas oil	205–250	400–480
Heavy gas oil	250–290	480–550
Atmospheric gas oil	260–315	500–800
Vacuum gas oil	425–600	800–1,100
Light vacuum gas oil	315–425	600–800
Heavy vacuum gas oil	425–600	425–1,110
Residuum	>510	>950

^a For convenience, boiling ranges which can vary from refinery to refinery are approximate and, for convenience, are converted to the nearest 5°. Also, there is overlap between some of the distillates because of the lack of a standard terminology that has been applied to these materials insofar as the terminology employed to name the fractions is either company dependent or refinery dependent.

^b Obtained in the “middle” boiling range which is on the order of 180–290 °C (355–550 °F) during the distillation process. The middle distillates are so named because the fractions are removed at mid-height of the distillation tower during the multistage process of thermal separation.

Thus, the term “crude oil” and the equivalent term “petroleum” cover a wide assortment of materials of different boiling range (Table 1.2) consisting of mixtures of hydrocarbon derivatives and other constituents that contain variable amounts of sulfur, nitrogen, and oxygen, which may vary widely in volatility, specific gravity, and viscosity (Table 1.3).

As a special note, and to avoid any apparent confusion that may arise from an inspection of the boiling ranges, the boiling ranges of the various distillate fraction from refinery distillation can vary from refinery to refinery and, as presented here (Table 1.2) are approximate and, for convenience, are converted to the nearest 5°. There is also an overlap between some of the distillates because of the lack of a standard terminology that has been applied to these materials insofar as the terminology employed for the fractions is either company dependent or refinery

Table 1.3 Hydrocarbon and Heteroatom Types in Crude Oil, Heavy Oil, and Tar Sand Bitumen

Class	Compound types
Saturated hydrocarbons	<i>n</i> -Paraffins <i>iso</i> -Paraffins and other branched paraffins Cycloparaffins (naphthenes) Condensed cycloparaffins (including steranes, hopanes) Alkyl side chains on ring systems
Unsaturated hydrocarbons	Olefins: nonindigenous Present in products of thermal reactions
Aromatic hydrocarbons	Benzene systems Condensed aromatic systems Condensed naphthene-aromatic systems Alkyl side chains on ring systems
Saturated heteroatomic systems	Alkyl sulfides Cycloalkyl sulfides
Sulfides	Alkyl side chains on ring systems
Aromatic heteroatomic systems	Furans (single-ring and multi-ring systems) Thiophenes (single-ring and multi-ring systems) Pyrroles (single-ring and multi-ring systems) Pyridines (single-ring and multi-ring systems) Mixed heteroatomic systems Amphoteric (acid–base systems) Alkyl side chains on ring systems

dependent. The middle distillates are those distillates and those fractions that occur in the “middle” boiling range which is on the order of 180–260 °C (355–500 °F) during the crude oil distillation process. The middle distillates are so named because the fractions are removed at mid-height of the distillation tower during the multistage process of thermal separation.

Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks (Gruse and Stevens, 1960; Speight, 1984). Because crude oil is a mixture of widely varying constituents and proportions, its physical

properties also vary widely and the color varies from colorless to black (Parkash, 2003; Gary et al., 2007; Speight, 2012a, 2014a; Hsu and Robinson, 2017; Speight, 2017).

Crude oil occurs in underground formations that are at various pressures depending on the depth and, because of the pressure, conventional crude oil typically contains considerable natural gas in solution. Crude oil underground is much more fluid than it is on the surface and is generally mobile under reservoir conditions because the elevated temperatures (the geothermal gradient) in subterranean formations decrease the viscosity. The geothermal gradient depths vary from site to site and from formation to formation but it is generally accepted to be on the order of 15 °F/1,000 ft or 120 °C/1,000 ft, i.e., 0.015 °C per foot of depth or 0.012 °C per foot of depth.

In the raw (unrefined) state, crude oil has minimal value, but when refined, it provides high-value liquid fuels, solvents, lubricants, and many other products (Purdy, 1957). The fuels derived from crude oil contribute approximately one-third to one-half of the total world energy supply and are used not only for transportation fuels (i.e., gasoline, diesel fuel, and aviation fuel, among others) but also to heat buildings. Crude oil products have a wide variety of uses that vary from gaseous and liquid fuels to near-solid machinery lubricants. In addition, the residue of many refinery processes, asphalt—a once-maligned by-product—is now a premium value product for highway surfaces, roofing materials, and miscellaneous waterproofing uses.

Crude oil is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation. And the terminology of these fractions has been bound by utility and often bears little relationship to composition.

Since there is a wide variation in the properties of crude oil (Table 1.4), the proportions in which the different constituents occur vary with origin (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). Thus, some crude oils have higher proportions of the lower boiling components and while other oils (such as heavy crude oil, extra heavy crude oil, and tar sand bitumen) have higher proportions of higher boiling components (usually referred to as the asphaltic components and the residuum) (Speight, 2014a, 2015a, 2017).

There is another type of crude oil that is recovered from shale formation and is generally referred to as “oil from tight shale.” This is a relatively new term to the crude oil lexicon and should not be confused with “shale oil,” which is oil produced by the thermal treatment of oil shale and the decomposition of the kerogen contained in the shale formation (Speight, 2012b).

The properties of oils from tight shale formations are significantly different to those of typical crude oils. Unlike most crude oils, shale oils are highly volatile, sweet (low-sulfur) liquids, with a high content of paraffin derivatives (alkanes)

Table 1.4 Examples of the Variation in the Properties of Crude Oil

Crude oil source	Specific gravity	API gravity	Residuum %v/v >535 °C (>1,000 °F)
United States			
California	0.858	33.4	23.0
Oklahoma	0.816	41.9	20.0
Pennsylvania	0.800	45.4	2.0
Texas	0.827	39.6	15.0
Other countries			
Bahrain	0.861	32.8	26.4
Iran	0.836	37.8	20.8
Iraq	0.844	36.2	23.8
Kuwait	0.860	33.0	31.9
Saudi Arabia	0.840	37.0	27.5
Venezuela	0.950	17.4	33.6

and low acidity. They also have minimal asphaltene (and resin) content phase and varying contents of filterable solids, hydrogen sulfide (H_2S), and mercaptans. There are significant differences in the sulfur content and the filterable solids loading. Solids loading (and the potential for inorganic fouling) of samples from a single producing region can be highly variable and associated with the stage of fracturing and production from which the oil is produced.

Finally, crude oil from tight shale formations may contain much higher levels of iron (Fe) than conventional crude oils (Benoit and Zurlo, 2014; De Graaf et al., 2014). In addition, other contaminant metals that promote the detrimental effects of iron (such as calcium, sodium, and potassium) are often present at elevated levels. Feedstocks with high iron content create a number of problems for refining and iron poisoning of fluid catalytic cracking catalyst occurs readily leading to: (1) an incase in slurry yield increases and (2) emission of sulfur oxides often increases. In the case of iron poisoning, activity and surface area tests are subject to artifacts that do not reveal that the catalyst is rendered inactive in the unit when the contact time with feed is short (contrary to the activity test unit).

1.3.1.2 Opportunity Crude Oil

While the term nonviscous feedstocks may suggest a highly suitable feedstock for a refinery, it may not be the case. In addition to conventional crude oil—often considered to be the prime refinery feedstocks—there are other types of crude

ones that are not always suitable for the refinery. Such feedstocks, which are occurring more often as refinery feedstocks, are (1) opportunity crude oil, (2) high-acid crude oil, and (3) foamy oil, all three of which can also be accommodated under the umbrella term “heavy crude oil.”

Thus, there is also the need for a refinery to be ready to accommodate opportunity crude oils and/or high-acid crude oils and/or foamy oils which, for many purposes, are often shipped to a refinery under the banner of heavy crude oil.

Opportunity crude oils are often dirty and need cleaning before refining by removal of undesirable constituents such as high-sulfur, high-nitrogen, and high-aromatics (such as polynuclear aromatic) components (Speight, 2014a, 2014b; Yeung, 2014).

More specifically, opportunity crude oils are either (1) new-to-the-refinery crude oils with unknown or poorly understood properties relating to processing issues or are (2) existing crude oils with well-known properties and processing concerns (Ohmes, 2014). Opportunity crude oils are often, but not always, heavy crude oils that are more difficult to process due to a high level of solids (and other contaminants) as well as a high level of acidity and a high viscosity. Opportunity crude oils (while cheaper to purchase because of the contaminants) may also (because of the heavy crude oil character) be incompatible with other (lighter crude oils) in the refinery feedstock blend and cause excessive equipment fouling when processed either in a blend or separately (Speight, 2014a, 2015b).

During the refinery process, fouling can occur in a variety of processes, usually inadvertently when the separation is detrimental to the process outcome (Speight, 2015b, 2017). Thus, separation of solids occurs whenever the solvent characteristics of the liquid phase are no longer adequate to maintain polar and/or high molecular weight constituents in solution.

Examples of such occurrences are: (1) separation of asphaltene constituents, which occurs when the paraffin nature of the liquid medium increases, (2) wax separation which occurs when there is a drop in temperature or the aromaticity of the liquid medium increases, and (3) sludge/sediment formation in a reactor which occurs (1) when the solvent characteristics of the liquid medium change so that asphaltic or wax materials separate or (2) when there is coke formation which occurs at high temperatures and commences when the solvent power of the liquid phase is not sufficient to maintain the coke precursors in solution, and (3) when there is sludge/sediment formation in fuel products which occurs because of the interplay of several chemical and physical factors.

In general, the foulant consists of organic material and/or inorganic material that is deposited by the feedstock at the time of (or shortly thereafter if there is an induction period) instability or incompatibility of the feedstock (one crude oil) with another during and shortly after a blending operation (Speight, 2014a, 2015b). However, fouling can also be a consequence of corrosion in a unit when deposits of inorganic solids become evident (Speight, 2015b). With the influx of

opportunity crudes, high-acid crudes, heavier crude oils, extra heavy crude oils, and tar sand bitumen into refineries (Chapter 1) fouling phenomena are more common and diverse (Speight, 2014a, 2014b, 2015b).

Fouling can be classified into two broad categories: (1) microfouling and (2) macrofouling. Common types of microfouling are: (1) biofouling, which is caused by microorganisms, (2) chemical reaction fouling, (3) precipitation fouling, (4) corrosion fouling, and (5) composite fouling, which is caused by more than one fouling mechanism or foulant. The occurrence of marine fouling typically occurs during the time when seaweed, bacteria, and other living organisms in the water adhere to immersed surfaces such as a ship hull which results in the formation of a layer that covers the surface thereby acting as a base for more material. In any case, the extent and severity of fouling is dependent on variables such as process parameter and the immediate environment.

On the other hand, macrofouling is caused by matter (or constituents) of either inorganic or organic origin, such as animals and plants. An example is the occurrence of fouling that occurs in heat transfer components in heat exchangers which can cause blockages or fretting damage. By way of explanation, *fretting* refers to wear damage as well as corrosion damage at the uneven (or rough) areas of metal surfaces and such damage is induced under load and in the presence of repeated relative surface motion, as induced for example by vibration which, as a result of contact with another surface, can cause mechanical wear and material transfer at the surface. This is often followed by the oxidation of both the metallic debris and the freshly exposed metallic surfaces. Typically, in many cases, the oxidized debris is much harder (and abrasive) than the surfaces from which it originated and often acts as an abrasive agent that increases the rate of both fretting and brinelling.

Briefly, fretting refers to wear and sometimes corrosion damage of loaded surfaces in contact while they encounter small oscillatory movements tangential to the surface. Fretting is caused by adhesion of contact surface asperities, which are subsequently broken again by the small movement. In addition, brinelling refers to mechanical wear which involves the permanent indentation of a hard surface.

Whatever the cause, fouling is a serious problem in the crude oil industry and is dependent on the properties of the feedstock (Table 1.5) and the properties are indicative of refinery performance and profitability (Ohmes, 2014). Therefore, understanding the properties and contaminants of various crude oils as well as the intermediate streams and final products is critical to selecting the crude slate for the refinery. In fact, the occurrence of fouling in reactors during processing has become more common with the influx of heavier feedstocks (such as heavy oil, extra heavy oil, and tar sand bitumen—tar sand bitumen is an exception insofar as it is not classed as a member of the crude oil family as defined by the United States Department of Energy) and the requirement of more complex processing units to convert such feedstocks into saleable products (Speight, 2014a).

Table 1.5 Feedstock Properties and Their Respective Impacts on Refining

Property	Comment	Impact
API	Low API gravity	High potential for coke formation Carbon deposition on catalyst Catalyst fouling and deactivation
Sulfur	Requires hydrogen for removal as hydrogen sulfide	Corrosion Catalyst fouling and deactivation
Nitrogen	Requires hydrogen for removal as ammonia	Corrosion Catalyst fouling and deactivation
Metals Ni/V/Fe	Typically associated with asphaltene fraction Require guard bed catalysts	Catalyst fouling and deactivation
Metals Na/Ca/Mg	Typically associated with high-acid crudes Require guard bed catalysts	Catalyst fouling and deactivation Corrosion Catalyst fouling and deactivation
Coke precursors	Require carbon rejection process	Catalyst fouling and deactivation
Asphaltene fraction	Increases potential for fouling	Phase separation during process Fouling Catalyst fouling and deactivation
Naphthenic acids	High levels cause corrosion	Corrosion and fouling
Compatibility	Certain crude blends are incompatible	Affects allowable blend behavior Phase separation Fouling
Chlorides	Typically associated with alkali metals	Corrosion Fouling
Viscosity	High viscosity	High potential for coke formation Phase separation during process Fouling

In addition to taking the necessary steps to process these feedstocks without serious fouling and any ensuing corrosion of the processing equipment, refiners need to develop programs for detailed feedstock evaluation in order to determine the quality of a feedstock so that the processing steps can be planned meticulously. For example, the compatibility of an opportunity crude oil not only with the viscous oils but also with other opportunity crude oils is an important aspect that should be considered prior to the onset of processing and to mitigate the possibility of any processing difficulties and the potential for equipment fouling (Speight, 2014a, 2015a).

Thus, before refining, there is the need for comprehensive evaluations of opportunity crude oils in order to make informed decisions regarding the suitability of an opportunity crude oil for a refinery.

1.3.1.3 High-Acid Crude Oil

High-acid crude oils are crude oils that contain considerable proportions of organic acid derivatives—commonly referred to as naphthenic acids—and, in many cases (but not all cases), high-acid crude oils are more viscous than the conventional crude oils (Speight, 2014a, 2014b). For convenience, the high-acid crude oils are presented in this section rather than within the section on “viscous feedstocks.”

By definition, a naphthenic acid is a monobasic carboxyl group attached to a saturated cycloaliphatic structure and the term naphthenic acid refers to a complex mixture of low molecular weight to high molecular weight acid derivatives as well as other acidic species (such as phenol derivatives). In fact, a major portion of the acidic constituents in a high acid feedstock may not be carboxylic acids and some of the constituents may be polycyclic and may have unsaturated bonds, aromatic rings, and hydroxyl groups. Some naphthenic acids may even contain heteroatoms other than the two oxygen atoms ($-\text{CO}_2\text{H}$) of the carboxylic acid group leading to a broad distribution of species.

High-acid crude oils cause corrosion in the refinery—corrosion is predominant at temperatures in excess of 180 °C (355 °F) (Ghoshal and Sainik, 2013)—and occur particularly in the atmospheric distillation unit (the first point of entry of the high-acid crude oil) and also in the vacuum distillation units (Speight, 2014b, 2014c). In addition, overhead corrosion is caused by the mineral salts, magnesium, calcium, and sodium chloride which are hydrolyzed to produce volatile hydrochloric acid, causing a highly corrosive condition in the overhead exchangers which can (and do, if ignored) present a significant contamination in opportunity crude oils. Other contaminants in the opportunity crude oils which are shown to accelerate the hydrolysis reactions include inorganic clay minerals and organic acid derivatives (Speight, 2014a, 2017, 2021).

In addition to taking preventative measure for the refinery to process these feedstocks without serious deleterious effects on the equipment, refiners will need to

develop programs for detailed and immediate feedstock evaluation so that they can understand the qualities of a crude oil very quickly and processing of such feedstocks can be planned meticulously (Speight, 2014a, 2017, 2021).

High-acid crude oils cause corrosion in the refinery—corrosion is predominant at temperatures in excess of 180 °C (355 °F) (Ghoshal and Sainik, 2013; Speight, 2014c)—and occurs particularly in the atmospheric distillation unit (the first point of entry of the high-acid crude oil) and also in the vacuum distillation units. In addition, overhead corrosion is caused by the mineral salts, magnesium, calcium, and sodium chloride which are hydrolyzed to produce volatile hydrochloric acid, causing a highly corrosive condition in the overhead exchangers. Therefore, these salts present a significant contamination in opportunity crude oils. Other contaminants in opportunity crude oils include inorganic clay minerals and organic acid derivatives which have the ability to accelerate the hydrolysis reactions.

In addition to taking preventative measure for the refinery to process these feedstocks without serious deleterious effects on the equipment, there is the need to develop programs that can be applied to feedstock evaluation so that the feedstock can be evaluated in terms of identification of the applicable necessary refinery operations (Speight, 2014a, 2015b, 2017).

1.3.1.4 Foamy Oil

Foamy oil is an oil-continuous foam that contains dispersed gas bubbles produced at the well head from heavy oil reservoirs under solution gas drive. The manner in which the gaseous constituents are dispersed in the oil distinguishes foamy oil behavior from conventional heavy crude oil. When the gas emerges from the solution in the reservoir, it does not coalesce into large gas bubbles or into a continuous flowing gas phase. Instead, it remains as small bubbles entrained in the oil, keeping the effective oil viscosity low while providing expansive energy that helps drive the oil toward the production. In addition, the crude oil known as “foamy oil” can contribute to unusually high production in heavy crude oil reservoirs and is considered to be solution-gas drive (Sun et al., 2013).

Thus, foamy oil is formed in a solution gas drive reservoir when gas is released from the oil due to a decrease in the reservoir pressure (Speight, 2014a, 2015b, 2017). In such cases, the oil appears at the wellhead of these heavy crude oil reservoirs as a foam, hence the term foamy oil. The gas initially exists in the form of small bubbles within individual pores in the rock but, as time passes and the pressure continues to decline, the bubbles grow to fill the pores. As the reservoir pressure continues to decrease, the gas bubbles created within the reservoir become sufficiently large to form a continuous gas phase. Once this occurs (i.e., when gas saturation exceeds the critical level—the minimum saturation at which a continuous gas phase exists in porous media), traditional two-phase (oil and gas) flow with

classical relative permeability occurs. As a result, the GOR increases rapidly after the critical gas saturation has been exceeded.

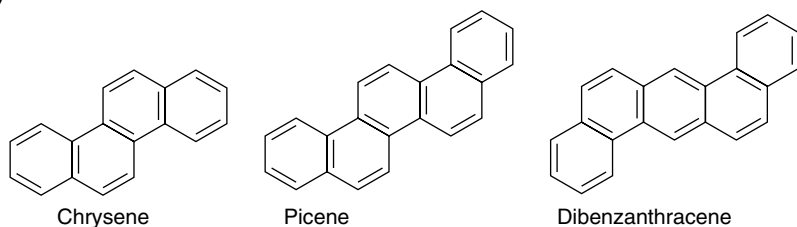
1.3.2 Viscous Feedstocks

Also, the viscous feedstocks are richer in polynuclear aromatic derivatives (Figure 1.7)—of which the peri-condensed system (Figure 1.7a) (in keeping with the structures of the precursor that eventually evolve to the crude oil derivatives) predominate over the kata-condensed systems (Figure 1.7b).

While the terminology used for the various refinery feedstocks has been described in detail elsewhere (Chapter 1) (Speight, 2021), for the sake of completeness and to mitigate the potential for any confusion or misunderstanding, a short description of the various viscous feedstocks is worthy of inclusion at this point.

As a general introduction, in the context of this book, a viscous feedstock typically has a relatively low proportions of volatile constituents (low molecular weight constituents) and high proportions of low volatility constituents (high molecular weight constituents). Thus, a viscous feedstock is comprised of complex assortment of different molecular and chemical types with high melting points and high pour points that greatly contribute to the poor fluid properties of the viscous feedstock and, hence, to low mobility (compared to conventional crude oil). The same is true for extra heavy oil and tar sand bitumen (Speight,

(a)



(b)

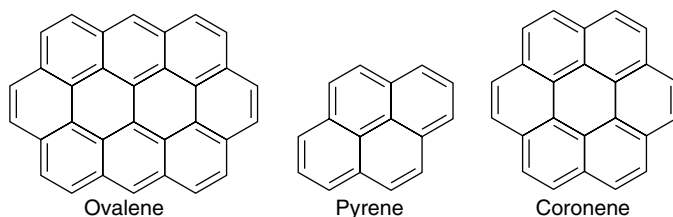


Figure 1.7 Examples of (a) peri-condensed and (b) kata-condensed aromatic systems.

2013b, 2013c, 2014a, 2019b). More generally a viscous feedstock typically has moderate-to-high levels of asphaltene constituents. The asphaltene constituents are not necessarily the primary cause for the high specific gravity (low API gravity) of the oil nor are they always the prime cause for production problems.

Briefly the asphaltene constituents are those constituents of oil that are insoluble in *n*-heptane or *n*-pentane while the resin constituents are those constituents of oil that are soluble in *n*-heptane or *n*-pentane but are adsorbed from these hydrocarbon solutions on to an adsorbent such as a clay mineral or alumina (Al_2O_3). In addition to the asphaltene constituents, it is also essential to consider the resin constituents and the aromatic constituents (especially the aromatic constituents that contain heteroatoms).

In the fractionation procedure (Figure 1.8), the hydrocarbon (*n*-pentane or *n*-heptane) must be specified since each liquid hydrocarbon gives different yield of the asphaltene fraction. Both the resin constituents and the asphaltene constituents produce coke in thermal processes (Speight, 2014a, 2017) and, therefore, are capable of interfering with refinery processes by means of the formation of sediment—a phenomenon known as instability or incompatibility (Chapter 10).

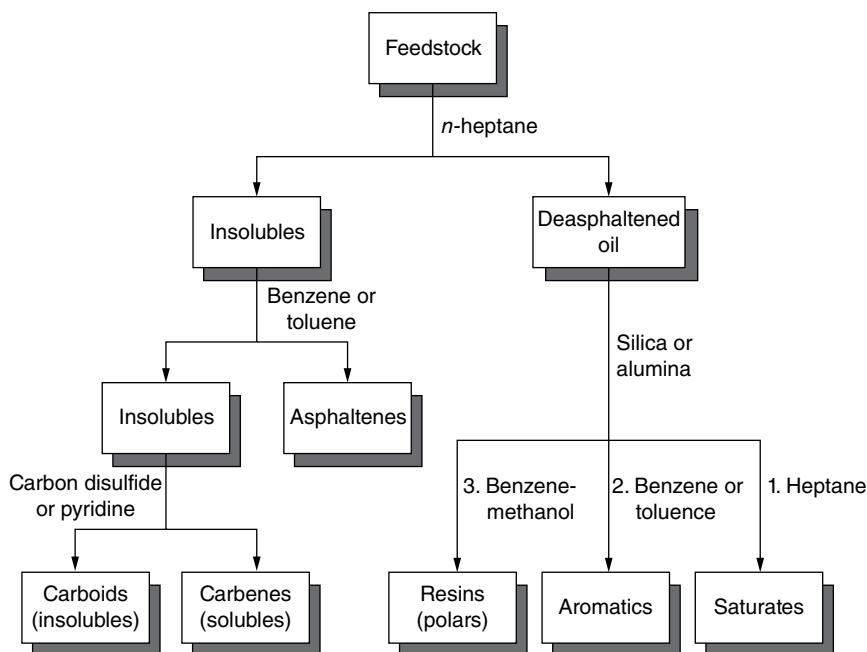


Figure 1.8 Schematic of the separation of oil into various bulk fractions.

1.3.2.1 Gas Oil

In the strictest sense, gas oil (Table 1.6) is not a member of the heavy oil family but the properties of this material often classify the gas oil as a viscous material from which lubricating oil and grease and cracked products can be manufactured (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017, 2021). In this respect, gas oil (especially the vacuum gas oil fraction) deserves to be given attention here.

Vacuum gas oil (often identified by the acronym VGO) is a for fluid catalytic cracker units and is used to produce distillates that may be employed as solvents or as blend stock for transportation fuels. On the basis of the product, the vacuum gas oil can be subdivided into (1) light vacuum gas oil, often identified by the acronym LVGO, and (2) heavy vacuum gas oil, often identified by the acronym HVGO.

Light vacuum gas oil is the lower boiling fraction of the vacuum gas oil while heavy vacuum gas oil is produced in the vacuum distillation unit (as the higher boiling fraction of the vacuum gas oil) through the distillation of the residuum (i.e., the nonvolatile fraction) from the atmospheric distillation column. The higher boiling fraction of the vacuum gas oil (the HVGO) is a heavy a complex

Table 1.6 Example of the Properties of Vacuum Gas Oil

Specific gravity at 60/60 °F	0.8739
Pour point (°C)	5
Viscosity at 37.8 °C, SSU	51.22
Viscosity at 98.8 °C, SSU	33.54
Aniline point (°C)	70
Molecular weight	278
Refractive index at 20 °C	1.4875
K_{uop} -factor	11.70
K_w -factor	11.67
ASTM distillation(D-86) (°C)	
IBP	265
10%	281
30%	304
50%	316
70%	334
90%	381
FBP	400

viscous fraction that is produced by vacuum distillation unit in the refinery as a black semisolid material that often has an odor similar to asphalt.

More generally, the heavy vacuum gas oil (HVGO) is that is produced as the lower side product from the vacuum distillation unit in a refinery. Vacuum gas oil has a boiling range on the order of (for example) 350–565 °C (660–1,050 °F) although this temperature range is subject to the refinery distillation parameters. More specifically, because the composition of the gas oil is dependent upon the source of the gas oil and there is no “typical composition” of a gas oil fraction, the maximum temperature at which cracking occurs is different for each gas oil and cannot be determined reliably. Nevertheless, vacuum gas oil is prone to thermal decomposition (cracking) at temperatures higher than 360 °C (680 °F) (Song et al., 2013; Wang et al., 2016). In many cases, the gas oil is mixed with hydrogen to suppress the cracking reactions that occur above the cracking temperature.

Finally, as a point of reference, there are two main uses of the vacuum gas oil which are (1) naphtha production, which is used as a gasoline blend stock—the heavy vacuum gas oil is sent to the fluidized catalytic cracking unit (often represented by the acronym FCU or FCCU) for conversion in the presence of a catalyst, to produce the desired product, and (2) kerosene production, which is used for production of diesel fuel—the heavy vacuum gas oil is sent to a hydrocracking unit where it is cracked to produce a mixture of products rich in middle distillates.

Briefly, the fluid catalytic cracking unit is one of the processes that is a type of secondary unit operation in the refinery plant. The technology is used for a high molecular weight hydrocarbon (such as the heavy vacuum gas oil) to convert the feedstock to valuable products such as naphtha (the prime product) and olefin gases using a high temperature and catalyst. In the process, the feedstock and the catalyst (in the form of a fluidized power) react in a reactor, and catalyst is regenerated and recycled (regenerator) (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017).

On the other hand, the vacuum gas oil may be sent to a hydrotreating unit which is used to remove impurities by using hydrogen to bind with sulfur (hydrodesulfurization, HDS), nitrogen (hydrodenitrogenation, HDN), and oxygen (hydrodeoxygenation, HDO). Thus, hydrotreating is a refining process for treating crude oil fractions from an atmospheric distillation unit or from a vacuum distillation unit (such as the heavy gas oil) in the presence of a catalyst and substantial quantities of hydrogen.

1.3.2.2 Heavy Crude Oil

The term heavy oil has also been arbitrarily used to describe both the heavy oil that require thermal stimulation of recovery from the reservoir and the bitumen in tar sand formation (i.e., bituminous sand formation) from which the bitumen is recovered by, for example, a mining operation (Speight, 2014a, 2019b).

When crude oil occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark to light colored liquid, it is often referred to as conventional crude oil (Table 1.7). Heavy crude oil is a type of crude oil that is different from the conventional crude oil insofar as they are much more difficult to recover from the subsurface reservoir (Speight, 2014a, 2019b). A heavy oil has a higher viscosity (and lower API gravity) than conventional crude oil, and primary recovery of the heavy oil requires thermal stimulation of the reservoir (Speight, 2017, 2019b).

Heavy crude oils are more difficult to recover from the subsurface reservoir than conventional crude oil. The definition of heavy crude oil has been (and continues to be) typically based on the API gravity or viscosity but the form of definition is arbitrary although there have been attempts to rationalize the definition based upon viscosity and API gravity (Speight, 2014a).

For many years, crude oil and heavy oil were very generally defined in terms of physical properties. For example, heavy oils were considered to be those crude oils that had gravity somewhat less than 20° API with the heavy oils falling into the API gravity range 10°–15°. For example, Cold Lake heavy crude oil has an API gravity equal to 12° and extra heavy oils, such as tar sand bitumen, usually have an API gravity in the range 5°–10° (Athabasca bitumen = 8° API). Residua would

Table 1.7 Example of the Properties of Heavy Crude Oil

		Heavy crude oil ^a
Whole oil	API gravity	12.0
	Carbon (% w/w)	84.5
	Hydrogen (% w/w)	12.1
	H/C atomic ratio	1.72
	Carbon (% w/w)	83.6
	Hydrogen (% w/w)	10.5
	Sulfur (% w/w)	3.84
	Nitrogen (% w/w)	0.31
	Oxygen	0.2
	Vanadium (ppm)	190
	Nickel (ppm)	70
	C5 asphaltenes	15.3
	C7 asphaltenes	7.8
	Conradson carbon residue (% w/w)	10.3

^a Cold Lake, Alberta, Canada.

vary depending upon the temperature at which distillation was terminated but usually vacuum residua are a range on the order of 2–8° API (Speight, 2000, 2014a).

Heavy crude oils have a much higher viscosity (and lower API gravity) than conventional crude oil, and primary recovery of these crude oil types usually requires thermal stimulation of the reservoir (Speight, 2014a, 2019b). The generic term “heavy crude oil” is often applied to a crude oil that has less than 20° API or less than 22° API or, in some cases, less than 25° API. Obviously, the use of the density-API descriptor is subject to variation depending on the company or the country or the limits of accuracy of the test method (by which the API was determined) and there is always the question that refers to the differences between a heavy crude oil having an API gravity of 19.5 and a heavy crude oil having an API gravity of 20.5 (Speight, 2014a, 2015a, 2019b). In addition, and to add further confusion to the so-called definition, heavy crude oil is often (a heavy crude oil having an API gravity of 19.5) described as having a sulfur content higher than 2% w/w (Speight, 2000, 2014a, 2017) and, in contrast to conventional crude oil, heavy crude oil is darker in color and may even be black.

Heavy crude oil is typically recognized as a type of crude oil but is different to the other types of crude oil insofar as heavy crude oil differs conventional crude oil (often referred to as light oil, i.e., low boiling low density) insofar as the heavy crude oil is more difficult to recover from the subsurface reservoir. The heavy crude oil has a higher viscosity (and lower API gravity) than conventional crude oil and recovery of heavy crude oil usually requires thermal stimulation of the reservoir leading to application of various thermal methods (such as coking) in the refinery for suitable conversion to low-boiling distillates.

There has been the continuing tendency to define heavy crude oil using the API gravity or viscosity, and the definition is quite arbitrary although there have been attempts to rationalize the definition based upon viscosity, API gravity, and density (Speight, 2014a, 2015a, 2019b, 2021). For example, heavy crude oil is considered to be the type of crude oils that had gravity somewhat less than 20° API with many heavy crude oils falling into the API gravity range 10°–15°. For example, Cold Lake heavy crude oil (Alberta, Canada) has an API gravity equal on the order of 12° and tar sand bitumen (Athabasca, Fort McMurray, Alberta, Canada) usually have an API gravity on the order of 5°–10° (Athabasca bitumen = 8° API). Using this scale, crude oil residua vary depending upon the temperature at which distillation was terminated but atmospheric residua are typically in the range 10°–15° API while vacuum residua are in the range 2°–8° API (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017, 2021).

In the simplest terms, heavy crude oil is a type of crude oil which is very viscous and does not flow easily. The common characteristic properties (relative to conventional crude oil) are high specific gravity, low hydrogen to carbon ratios, high carbon residues, and high contents of asphaltenes, heavy metals (i.e., metallic

chemical elements that have a relatively high density and are toxic or poisonous at low concentrations; examples of heavy metals include [alphabetically]: arsenic, As, cadmium, Cd, chromium, Cr, mercury, Hg, lead, Pb, and thallium, Tl), sulfur, and nitrogen. Specialized refining processes are required to produce more useful fractions, such as: naphtha, kerosene, gas oil, and wax.

Thus, the term heavy crude oil has also been arbitrarily used to describe the viscous crude oil that requires a thermal stimulation method to recover the oil from the reservoir. It must also be remembered that the term “heavy crude oil” may also include opportunity crude oil, high-acid crude oil, and foamy oil and, thus, there is the need for a refinery to be ready to accommodate opportunity crude oils and/or high-acid crude oils and/or foamy oils which, for many purposes, may have been shipped to a refinery under the banner of “heavy crude oil.”

1.3.2.3 Extra Heavy Crude Oil

Extra heavy oil is a nondescript term (related to viscosity) of little scientific meaning, which is usually applied to tar sand bitumen, which is generally incapable of free flow under reservoir conditions. Thus, the term extra heavy oil is used to describe materials that occur in the solid or near-solid state in the deposit or reservoir and are generally incapable of free flow under ambient conditions. Whether or not such a material exists in the near-solid or solid state in the reservoir can be determined from the pour point and the reservoir temperature (Tables 1.8 and 1.9).

The general difference is that extra heavy oil, which may have properties similar to tar sand bitumen in the laboratory under ambient conditions of temperature and pressure (e.g., the API gravity is on the order of 8, the sulfur content is on the order of 4.8% w/w, and the C5 asphaltene content is on the order of 17% w/w as well as other properties that are similar to the properties of tars and bitumen) but unlike tar sand bitumen in the deposit, the extra heavy crude oil exhibits mobility in the reservoir or deposit (Speight, 2014a, 2019b, 2021). Thus, extra heavy oil can flow at the reservoir temperature and can be produced without additional viscosity-reduction techniques through variants of conventional processes such as long horizontal wells, or multilateral arrangement of the production wells.

This is the case, for instance, in the Orinoco basin (Venezuela) or in offshore reservoirs of the coast of Brazil but, once outside of the influence of the high reservoir temperature, these oils are too viscous at surface to be transported through conventional pipelines and require heated pipelines for transportation. Alternatively, the oil must be partially upgraded or fully upgraded or diluted with a low boiling (low density) hydrocarbon (such as aromatic naphtha) to create a mix that is suitable for transportation (Speight, 2014a, 2017).

Thus, extra heavy oil is a material that occurs as in fluid at the high temperature of the reservoir-deposit and, thus, has mobility under temperature conditions in the reservoir-deposit insofar as the temperature of the reservoir-deposit is higher

Table 1.8 Simplified Differentiation Between Conventional Crude Oil, Tight Oil, Heavy Crude Oil, Extra Heavy Crude Oil, and Tar Sand Bitumen^a

<i>Conventional Crude Oil</i>
Mobile in the reservoir
API gravity: >20°
Primary recovery methods
Secondary recovery methods
<i>Heavy Crude Oil</i>
More viscous than conventional crude oil
API gravity: 10–20°
Mobile in the reservoir
Secondary recovery methods
Tertiary recovery (enhanced oil recovery—EOR, e.g., steam stimulation)
<i>Extra Heavy Crude Oil</i>
Similar properties to the properties of tar sand bitumen
API gravity: <10°
Temperature of the reservoir/deposit higher than pour point of the oil
Mobile in the reservoir/deposit
Secondary recovery methods
Tertiary recovery methods (enhanced oil recovery—EOR, e.g., steam stimulation)
<i>Tar Sand Bitumen</i>
API gravity: <10°
Temperature of the reservoir/deposit lower than pour point of the oil
Immobile in the deposit
Mining (often preceded by explosive fracturing)
Extreme heating methods
Innovative methods ^b
<i>Residuum</i>
Semi-mobile to immobile at ambient conditions
Typically, API gravity: 5–15°; sulfur: 2.0–5.0% w/w; metals: 100–1,000 ppm
Does not occur naturally; manufactured product produced in a refinery
Atmospheric residuum: source of heavy gas oil under vacuum distillation
Vacuum residuum: nonvolatile under vacuum distillation conditions
Typically immobile under ambient conditions

^a This list is not intended for use as a means of classification.

^b Innovative methods exclude tertiary recovery methods and methods such as steam-assisted gravity drainage (SAGD) and vapor-assisted extraction (VAPEX) as well as variants or hybrids thereof (Speight, 2016).

Table 1.9 Use of Pour Point and Reservoir/Deposit Temperature to Differentiate Between Heavy Crude Oil, Extra Heavy Crude Oil, and Tar Sand Bitumen

Oil	Location	Temperature	Effect on oil
Heavy crude oil	Reservoir or deposit	Higher than oil pour point	Fluid
			Mobile
	Surface/ambient	Higher than oil pour point	Fluid
Extra heavy crude oil	Reservoir or deposit	Higher than oil pour point	Mobile
			Fluid
	Surface/ambient	Lower than oil pour point	Solid to near-solid
			Fluidity much reduced
Tar sand bitumen	Reservoir or deposit	Lower than oil pour point	Immobile
			Solid to near-solid
			Not fluid
	Surface/ambient	Lower than oil pour point	Immobile
			Solid to near-solid
			Not fluid
			Immobile

than the pour point of the oil. While this type of oil may resemble tar sand bitumen and does not flow easily, extra heavy oil is generally recognized as having mobility in the reservoir compared to tar sand bitumen, which is typically incapable of mobility (free flow) under reservoir conditions. For example, the tar sand bitumen located in Alberta, Canada, is not mobile in the deposit and requires extreme methods of recovery to recover the bitumen. On the other hand, much of the extra heavy oil located in the Orinoco basin of Venezuela requires recovery methods that are less extreme because of the mobility of the material in the reservoir. Whether the mobility of extra heavy oil is due to a high reservoir temperature (i.e., the reservoir temperature is higher than the pour point of the extra heavy oil) or subject to other factors due to localized conditions in the reservoir. This may also be reflected in the choice of suitable conversion process for extra heavy crude oil or for tar sand bitumen in the refinery.

In the context of this book, the methods outlined in this book for refining viscous feedstocks focus on heavy oil with an API gravity of less than 20 with a variable sulfur content (which includes atmospheric residua and vacuum residua) (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017). However, it must be recognized that some of the heavy oil are sufficiently liquid to be recovered by pumping operations and are already being recovered by this method. Refining depends on the characteristics (properties) since these heavy oils fall into a range of high viscosity and the viscosity is subject to temperature effects (Speight, 2001, 2014a, 2015a), which is the reason for the application of thermal conditions or dilution with a suitable solvent (such as aromatic naphtha) to enable heavy oil to flow in pipeline or within the refinery system.

1.3.2.4 Tar Sand Bitumen

In addition to heavy crude oil and the so-called extra heavy crude oil, there remains an even more viscous material (Table 1.10) that offers some relief to the potential shortfalls in supply (Meyer and De Witt, 1990; Speight, 2014a, 2016). This is the bituminous material that is found in tar sand (oil sand) deposits (referred to as oil sand deposits in Canada). However, many of these reserves are only available with some difficulty due to the highly viscous nature of the bitumen (because of the substantial differences in character between conventional crude oil and tar sand bitumen) and optional refinery scenarios are necessary for conversion of the

Table 1.10 Examples of the Properties of Tar Sand Bitumen

Property	Athabasca (Alberta, Canada)	Sunnyside (Utah, USA)
Specific gravity	1.03	1.015
API gravity	6.5	7.9
Viscosity (cP)		
38 °C/100 °F	750,000	1,500,000
Pour point (°F)	50	75
Elemental analysis (% w/w)		
Carbon	83.0	86.8
Hydrogen	10.6	10.8
Nitrogen	0.5	1.1
Sulfur	4.9	0.7
Oxygen (by difference)	1.0	0.6
Composition (% w/w)		
C5 Asphaltenes	17.0	23.7
Carbon residue (% w/w)		
Conradson	14.0	15.0

bitumen to liquid products (Speight, 2000, 2014a, 2016, 2021). Tar sand deposits, also variously called oil sand deposits or bituminous sand deposits, vary from a loose sandstone formation to a consolidated sandstone formation or a porous carbonate rock formation, that is, impregnated with bitumen in the form of a viscous asphaltic oil that has an extremely high viscosity under reservoir conditions.

The term “tar sand bitumen” (also, on occasion, incorrectly referred to as native asphalt) includes a wide variety of near-black to black materials that occur in the form of near-solid to solid in the deposit either (1) with no mineral impurity or (2) with a mineral matter content that may exceed 50% w/w. Bitumen is frequently found filling pores and crevices of sandstone, limestone, or argillaceous sediments, in which case the organic and associated mineral matrix is known as rock asphalt. Even though the term tar sand is incorrect since tar is a product of the thermal processing of coal (Speight, 2013a), the term has remained in use. Also, it is incorrect to refer to native bituminous materials as tar or pitch even though the word “tar” is descriptive of the black, nonvolatile bituminous material, it is best to avoid its use with respect to natural materials and to restrict the meaning to the volatile or near-volatile products produced in the destructive distillation of such organic substances as coal (Speight, 2013a). In the simplest sense, pitch is the distillation residue of the various types of tar. Thus, alternative names, such as bituminous sand or oil sand, are gradually finding usage, with the former name (bituminous sands) more technically correct. The term oil sand is also used in the same way as the term tar sand, and these terms are used interchangeably throughout this text.

The permeability of a tar sand deposit is low and passage of fluids through the deposit can only be achieved by prior application of fracturing techniques. Alternatively, bitumen recovery can be achieved by conversion of the bitumen to a product in situ (often referred to as in situ upgrading) followed by product recovery from the deposit (Speight, 2013b, 2013c, 2014a, 2016, 2019b). The bitumen is a high-boiling material with little, if any, material boiling below 350 °C (660 °F) and the boiling range approximates the boiling range of an atmospheric residuum (Speight, 2014a, 2015a, 2019b).

There have been many attempts to define tar sand deposits and the bitumen contained therein. In order to define conventional crude oil, heavy oil, and bitumen, the use of a single physical parameter such as viscosity is not sufficient. Other properties such as API gravity, elemental analysis, composition, and, most of all, the properties of the bulk deposit must also be included in any definition of these materials. In fact, the most appropriate definition of tar sands is found in the writings of the United States government (Speight, 2014a, 2016):

Tar sands are the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques.

This definition refers to the character of the bitumen through the method of recovery. Mining methods match the requirements of this definition (since mining is not one of the specified recovery methods) and the bitumen can be recovered by alteration of its natural state such as thermal conversion to a product that is then recovered. In this sense, changing the natural state (the chemical composition) as occurs during several thermal processes (such as some in-situ combustion processes) also matches the requirements of the definition.

By inference and by omission, conventional crude oil and heavy crude oil are also included in this definition. Crude oil is the material that can be recovered by conventional oil well production methods whereas heavy oil is the material that can be recovered by enhanced recovery methods. Tar sand is currently recovered by a mining process followed by separation of the bitumen by the hot water process. The bitumen is then used to produce hydrocarbon derivatives by a conversion process.

The only commercial operations for the recovery of bitumen from tar sand and its subsequent conversion to liquid fuels exist in the Canadian Province of Alberta where Suncor (initially as Great Canadian Oil Sands before the name change) went onstream in 1967 and Syncrude (a consortium of several companies) went onstream in 1977. Thus, throughout this text, frequent reference is made to tar sand bitumen, but because commercial operations have been in place for approximately 50 years, it is not surprising that more is known about the Alberta (Canada) tar sand reserves than any other reserves in the world. Therefore, when discussion is made of tar sand deposits, reference is made to the relevant deposit, but when the information is not available, the Alberta material is used for the purposes of the discussion.

Refining heavy crude oil, extra heavy crude oil, tar sand bitumen, and residua depends to a large degree on the composition of the feedstock and there are wide differences in properties between, say, tar sand bitumen and conventional crude oil (Table 1.11) (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017). Generally, the bitumen found in tar sand deposits is an extremely viscous material that is immobile and cannot be refined by the application of conventional refinery. On the other hand, extra heavy oil, which is often likened to tar sand bitumen because of similarities in the properties of the two, has a degree of mobility under reservoir or deposit conditions but typically suffers from the same drawbacks as the immobile bitumen in refinery operations.

Thus, alternative names, such as bituminous sand or oil sand, are gradually finding usage, with the former name (bituminous sands) more technically correct. The term oil sand is also used in the same way as the term tar sand, and these terms are used interchangeably throughout this text.

Bituminous rock and bituminous sand are those formations in which the bituminous material is found as a filling in veins and fissures in fractured rocks or impregnating relatively shallow sand, sandstone, and limestone strata. The deposits contain as much as 20% bituminous material, and if the organic material in the

Table 1.11 Comparison of the Properties of Conventional Crude Oil and Tar Sand Bitumen

Property	Bitumen (Athabasca)	Crude oil
Specific gravity	1.03	0.85–0.90
Viscosity (cP)		
38 °C/100 °F	750,000	<200
100 °C/212 °F	11,300	
Pour point (°F)	>50	<32
Elemental analysis (% w/w)		
Carbon	83.0	86.0
Hydrogen	10.6	13.5
Nitrogen	0.5	0.2
Oxygen	0.9	ca. 0.5
Sulfur	4.9	ca. 2.0
Ash	0.8	0.0
Nickel (ppm)	250	ca. 10.0
Vanadium (ppm)	100	ca. 10.0
Composition (% w/w)		
Asphaltenes (pentane)	17.0	<10.0
Resins	34.0	<20.0
Aromatics	34.0	ca. 30.0
Saturates	15.0	ca. 30.0
Carbon residue (% w/w)		
Conradson	14.0	<10.0

rock matrix is bitumen, it is usual (although chemically incorrect) to refer to the deposit as rock asphalt to distinguish it from bitumen that is relatively mineral free. A standard test method (ASTM D4, 2021) is available for determining the bitumen content of various mixtures with inorganic materials, although the use of word bitumen as applied in this test might be questioned and it might be more appropriate to use the term organic residues to include tar and pitch. If the material is the asphaltite-type or asphaltoid-type, the corresponding terms should be used: rock asphaltite or rock asphaltoid.

Bituminous rocks generally have a coarse, porous structure, with the bituminous material in the voids. A much more common situation is that in which the organic material is present as an inherent part of the rock composition insofar as

it is a diagenetic residue of the organic material detritus that was deposited with the sediment. The organic components of such rocks are usually refractory and are only slightly affected by most organic solvents.

Tar sand deposits occur throughout the world and the largest deposits occur in Alberta, Canada (the Athabasca, Wabasca, Cold Lake, and Peace River areas), and in Venezuela. Smaller deposits occur in the United States, with the larger individual deposits in Utah, California, New Mexico, and Kentucky. The term tar sand, also known as oil sand (in Canada), or bituminous sand, commonly describes sandstones or friable sand (quartz) impregnated with a viscous organic material known as bitumen (a hydrocarbonaceous material that is soluble in carbon disulfide). Significant amounts of fine material, usually largely or completely clay, are also present. The degree of porosity in tar sand varies from deposit to deposit and is an important characteristic in terms of recovery processes for the bitumen which is the desirable fraction of the tar sand and from which a variety of distillable products can be produced (Speight, 2014a, 2017). However, the bitumen is usually not recoverable by conventional crude oil production techniques (Speight, 2013b, 2013c, 2014a, 2016).

The properties and composition of the tar sand deposits and the bitumen contained therein significantly influence the selection of recovery and the bitumen conversion processes and vary among the bitumen from different deposits. In the so-called wet sands or water-wet sands of the Athabasca deposit, a layer of water surrounds the sand grain, and the bitumen partially fills the voids between the wet grains. The Utah tar sand deposits typically lack the water layer and the bitumen is in direct contact with the sand grains and, without any intervening water; such tar sands are typically sometimes referred to as oil-wet sands.

Typically, more than 99% w/w of mineral matter is composed of quartz and clay minerals—the latter are detrimental to refining operations. The typical composition of the P.R. Spring (also written as Peor Spring) tar sand area has a porosity on the order of 8.4% v/v with the solid/liquid fraction typically being on the order of 90.5% w/w sand, 1.5% w/w fines, 7.5% w/w bitumen, and 0.5% w/w water. The high concentration of heteroatoms (nitrogen, oxygen, sulfur, and metals) contribute to (1) an increase the viscosity of the bitumen, (2) an increase in the bonding of bitumen with the minerals, (3) a reduced yield of recovered bitumen, and (4) difficulties encountered during processing of the bitumen.

Finally, as an addition to this subsection and for information purposes, synthetic crude oil is produced by upgrading bitumen to reduce its density and viscosity for transport by pipeline (Speight, 2014a, 2017). A disadvantage to this concept is that supplies of synthetic crude oils are limited by the availability of upgraders at the source of the extraction of the bitumen from the tar sand and that a mixture on the order of 50% v/v and 50% v/v synthetic crude oil is required to obtain the desired density and viscosity.

1.3.2.5 Residuum

In contrast to the naturally occurring heavy crude oil, extra heavy crude oil, and tar sand bitumen, a residuum (pl. residua, also shortened to resid, pl. resids) is a manufactured material (rather than a naturally occurring material) insofar as a residuum is produced as a result of crude oil refining (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017). Thus:

Feedstock	Atmospheric distillation
	Naphtha
	Kerosene
	Middle distillates
	Atmospheric gas oil
	Atmospheric residuum
Atmospheric residuum	Vacuum distillation
	Gas oil
	Light gas oil
	Heavy gas oil
	Vacuum residuum

In addition, the properties are variable depending upon the cut point (i.e., either atmospheric residua or vacuum residua) (Table 1.12) (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017). Many residua are subject to further refining after production and are worthy of mention here as optional refinery viscous feedstocks either further refined as single feedstocks or as blends with other feedstocks, such as gas oil, as well as conventional whole crude oil, heavy crude oil, extra heavy crude oil, and tar sand bitumen.

Typically, a residuum is the residue obtained from crude oil after nondestructive distillation has removed all the volatile materials. The temperature of the distillation is usually maintained below 350 °C (660 °F) since the rate of thermal decomposition of crude oil constituents is minimal below this temperature but the rate of thermal decomposition of crude oil constituents is substantial above 350 °C (660 °F). If the temperature of the distillation unit rises above 350 °C (660 °F) as happens in certain units where temperatures up to 395 °C (740 °F) are known to occur, cracking can be controlled by adjustment of the residence time.

Residua (pl: residuum, often shortened to “resid”) are black, viscous materials that are obtained by distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum) and the properties of the residuum do vary with the initial boiling point of the residuum (Table 1.13) (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and

Table 1.12 Properties of Residua Showing the Differences Between Atmospheric Residua (650° Resids) and Vacuum Residua (1,050° Resids)

Feedstock	Gravity API	Sulfur (wt%)	Nitrogen (wt%)	Nickel (ppm)	Vanadium (ppm)	Asphaltenes (heptane) (wt%)	Carbon residue (Conradson) (wt%)
Arabian light, >650 °F	17.7	3.0	0.2	10.0	26.0	1.8	7.5
Arabian light, >1,050 °F	8.5	4.4	0.5	24.0	66.0	4.3	14.2
Arabian heavy, >650 °F	11.9	4.4	0.3	27.0	103.0	8.0	14.0
Arabian heavy, >1,050 °F	7.3	5.1	0.3	40.0	174.0	10.0	19.0
Alaska, North Slope, >650 °F	15.2	1.6	0.4	18.0	30.0	2.0	8.5
Alaska, North Slope, >1,050 °F	8.2	2.2	0.6	47.0	82.0	4.0	18.0
Lloydminster (Canada), >650 °F	10.3	4.1	0.3	65.0	141.0	14.0	12.1
Lloydminster (Canada), >1,050 °F	8.5	4.4	0.6	115.0	252.0	18.0	21.4
Kuwait, >650 °F	13.9	4.4	0.3	14.0	50.0	2.4	12.2
Kuwait, >1,050 °F	5.5	5.5	0.4	32.0	102.0	7.1	23.1
Tia Juana, >650 °F	17.3	1.8	0.3	25.0	185.0		9.3
Tia Juana, >1,050 °F	7.1	2.6	0.6	64.0	450.0		21.6
Taching, >650 °F	27.3	0.2	0.2	5.0	1.0	4.4	3.8
Taching, >1,050 °F	21.5	0.3	0.4	9.0	2.0	7.6	7.9

Note: >650 °F⁺ to >1,050 °F⁺ is accompanied by: (1) decrease in API gravity, (2) increase in sulfur content, (3) increase in nitrogen content, (4) increase in nickel content, (5) increase in vanadium content, (6) increase in asphaltene content, and (7) increase in carbon residue.

Table 1.13 Properties of Tia Juana Crude Oil and the Different Residua

	Whole crude	Residua		
		650 °F+	950 °F+	1,050 °F+
Yield (vol%)	100.0	48.9	23.8	17.9
Sulfur (wt%)	1.08	1.78	2.35	2.59
Nitrogen (wt%)		0.33	0.52	0.60
API gravity	31.6	17.3	9.9	7.1
Carbon residue (wt%) Conradson		9.3	17.2	21.6
Metals (ppm)				
Vanadium		185		450
Nickel		25		64
Viscosity				
Kinematic				
At 100 °F	10.2	890		
At 210 °F		35	1,010	7,959
Furol				
At 122 °F		172		
At 210 °F			484	3,760
Pour point (°F)	−5	45	95	120

Robinson, 2017; Speight, 2017). More typically, residua are black, viscous materials that may be near liquid at room temperature (typically, an atmospheric residuum) or solid (typically, a vacuum residuum) depending upon the properties of the crude oil source.

When a residuum is obtained from a feedstock and thermal decomposition has commenced, it is more usual to refer to this product as cracked residuum (sometimes referred to as pitch, a name derived from the coal industry). The differences between conventional crude oil and the related residua are due to the relative amounts of various constituents present, which are removed or retained by according to the relative volatility of the constituents.

The vacuum residuum (also commonly referred to as “vacuum bottoms,” typically 950 °F⁺ or 1050 °F⁺) is the most complex of crude oil and, in many cases, may even resemble heavy oil or extra heavy oil or tar sand bitumen in composition. Vacuum residua contain the majority of the heteroatoms originally in the crude oil and molecular weight of the constituents range up to several thousand (as near as can be determined but subject to method dependence). The fraction is

so complex that the characterization of individual species is virtually impossible, no matter what claims have been made or will be made. Separation of vacuum residua by group type can be difficult because of the multi-substitution of aromatic and naphthenic species as well as by the presence of multiple functionalities in single molecules (Chapters 2 and 3) (Speight, 2014a, 2021).

Typically, the precipitation of the asphaltene fraction *n*-pentane or *n*-heptane is used as the initial step for the characterization of a viscous feedstock, such as a vacuum residuum (Chapter 3) (Speight, 2014a, 2015a). The insoluble fraction, the pentane–asphaltene fraction or the heptane–asphaltene fractions, may be as much as 50% by weight of a vacuum residuum. The pentane-soluble or the heptane-soluble portion (often referred to as the maltene fraction) of the residuum is then fractionated by adsorption chromatographically into several solubility or adsorption classes for characterization (Chapter 3). However, in spite of claims to the contrary, the method is not a separation by chemical type. However, the separation of the asphaltene fraction does, however, provide a simple way to remove some of the highest molecular weight and most polar components but the asphaltene fraction is so complex that compositional detail based on average parameters is of questionable value.

For the 565 °C⁺ (1050 °F⁺) fractions of crude oil, the levels of nitrogen and oxygen may begin to approach the concentration of sulfur. These elements consistently concentrate in the most polar fractions to the extent that every molecule contains more than one heteroatom. At this point, structural identification is somewhat fruitless and characterization techniques are used to confirm the presence of the functionalities found in lower boiling fractions such as, for example, acid derivatives, phenol derivatives, nonbasic (carbazole-type) nitrogen derivatives, and basic (quinoline-type) nitrogen derivatives (Speight, 2014a).

The nickel and vanadium that are concentrated into the vacuum residuum appear to occur in two forms: (1) porphyrins and (2) non-porphyrins. Because the metalloporphyrins can provide insights into crude oil maturation processes, they have been studied extensively and several families of related structures have been identified. On the other hand, the non-porphyrin metals remain not clearly identified although some studies suggest that some of the metals in these compounds still exist in a tetra-pyrrole (porphyrin-type) environment.

It is more than likely that, in a specific residuum molecule, the heteroatoms are arranged in different functional types thereby contributing to an extremely complex fraction. Thus, considering the potential (and the reality) for the number of different combinations that are possible, the chances of determining every structure in a residuum are minimal. Because of this seemingly insurmountable task, it may be better to determine ways of utilizing the residuum rather attempting to determine (at best questionable) molecular structures.

In summary, the chemical composition of a residuum is complex. Physical methods of fractionation usually indicate high proportions of asphaltene

constituents and resin constituents, even in amounts up to 50% (or higher) of the residuum (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017). In addition, the presence of ash-forming metallic constituents, including such organometallic compounds as those of vanadium and nickel, is also a distinguishing feature of residua and the heavier oils. Furthermore, the deeper the cut into the crude oil, the greater is the concentration of sulfur and metals in the residuum and the greater the deterioration in physical properties.

1.3.2.6 Asphalt

Although not a naturally occurring material but manufactured from crude oil and any of the viscous feedstocks as a black or brown material that has a consistency varying from a viscous liquid to a glassy solid, a description of the production of asphalt in the refinery is warranted to dismiss any potential confusion between a residuum and asphalt (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2016; Hsu and Robinson, 2017; Speight, 2017).

Put simple, asphalt is produced simply by distillation of a feedstock to produce a nonvolatile product which can be referred to as residual asphalt or straight run asphalt—straight run asphalt, like any other straight run product—refers to the product that emerges from the refinery distillation column.

Feedstock [distillation]	Residuum
Residuum + [aerial oxidation]	Asphalt ^a
Asphalt [+ solvent]	Cutback asphalt

^a Often referred simply to as “oxidized asphalt” or “blown asphalt.”

However, in addition to this simplified manufacturing outline, if the asphalt is prepared by the solvent extraction method in which a residuum is subject to extraction by a low boiling liquid hydrocarbon (such as propane) or if blown or otherwise treated, the term should be modified accordingly to qualify the product (e.g., “propane asphalt,” “blown asphalt”).

In very general terms, asphalt may often resemble bitumen, hence the tendency to refer to bitumen (incorrectly) as native asphalt. It is recommended that there is a differentiation between asphalt (manufactured) and bitumen (naturally occurring) other than by use of the qualifying terms crude oil and native bitumen (i.e., the native or naturally occurring material) and asphalt (i.e., the manufactured material) in a way that reflects the origins of each of the materials which is also reflected in the chemical properties and physical properties of the two types of materials.

Furthermore, it advantages (if not necessary) to distinguish between the asphalt which originates from crude oil by refining and the product in which the source of the asphalt is a material other than crude oil, such as wurtzilite asphalt or

gilsonite asphalt (Bland and Davidson, 1967; Speight, 2014a, 2016). In the absence of a qualifying word, it should be assumed that the term asphalt refers the product manufactured from crude oil and has satisfied the properties as specified in the standard test methods, some of which are applicable to compare the properties of asphalt that has been spilled into an ecosystem on a before-and-after basis (Table 1.14) (ASTM, 2021).

Table 1.14 Examples of ASTM Standard Test Methods for Asphalt and Pitch

Number	Title
ASTM D4	Standard Test Method for Bitumen Content
ASTM D5	Standard Test Method for Penetration of Bituminous Materials
ASTM D6	Standard Test Method for Loss on Heating of Oil and Asphaltic Compounds
ASTM D20	Standard Test Method for Distillation of Road Tars
ASTM D36	Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)
ASTM D56	Standard Test Method for Flash Point by Tag Closed Cup Tester
ASTM D61	Standard Test Method for Softening Point of Pitches (Cube-in-Water Method)
ASTM D70	Standard Test Method for Density of Semi-Solid Bituminous Materials (Pycnometer Method)
ASTM D88	Standard Test Method for Saybolt Viscosity
ASTM D92	Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester
ASTM D93	Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester
ASTM D94	Standard Test Methods for Saponification Number of Petroleum Products
ASTM D95	Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation
ASTM D113	Standard Test Method for Ductility of Bituminous Materials
ASTM D129	Standard Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)
ASTM D139	Standard Test Method for Float Test for Bituminous Materials
ASTM D140	Standard Practice for Sampling Bituminous Materials
ASTM D189	Standard Test Method for Conradson Carbon Residue of Petroleum Products
ASTM D244	Standard Test Methods and Practices for Emulsified Asphalts

Table 1.14 (Continued)

Number	Title
ASTM D524	Standard Test Method for Ramsbottom Carbon Residue of Petroleum Products
ASTM D1370	Standard Test Method for Contact Compatibility Between Asphaltic Materials (Oliensis Test)
ASTM D1552	Standard Test Method for Sulfur in Petroleum Products (High Temperature Method)
ASTM D1669	Standard Practice for Preparation of Test Panels for Accelerated and Outdoor Weathering of Bituminous Coatings
ASTM D1754	Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)
ASTM D2042	Standard Test Method for Solubility of Asphalt Materials in Trichloroethylene
ASTM D2170	Standard Test Method for Kinematic Viscosity of Asphalts (Bitumens)
ASTM D2171	Standard Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer
ASTM D2319	Standard Test Method for Softening Point of Pitch (Cube-in-Air Method)
ASTM D2397	Standard Specification for Cationic Emulsified Asphalt
ASTM D2622	Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
ASTM D2872	Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)
ASTM D3104	Standard Test Method for Softening Point of Pitches (Mettler Softening Point Method)
ASTM D3142	Standard Test Method for Specific Gravity, API Gravity, or Density of Cutback Asphalts by Hydrometer Method
ASTM D3143	Standard Test Method for Flash Point of Cutback Asphalt with Tag Open-Cup Apparatus
ASTM D3279	Standard Test Method for <i>n</i> -Heptane Insolubles
ASTM D3461	Standard Test Method for Softening Point of Asphalt and Pitch (Mettler Cup-and-Ball Method)
ASTM D4045	Standard Test Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry
ASTM D4055	Standard Test Method for Pentane Insolubles by Membrane Filtration
ASTM D4072	Standard Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch

(Continued)

Table 1.14 (Continued)

Number	Title
ASTM D4124	Standard Test Method for Separation of Asphalt into Four Fractions
ASTM D4287	Standard Test Method for High-Shear Viscosity Using a Cone/Plate Viscometer
ASTM D4294	Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
ASTM D4312	Standard Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch (Short Method)
ASTM D4402	Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer
ASTM D4469	Standard Practice for Calculating Percent Asphalt Absorption by the Aggregate in an Asphalt Pavement Mixture
ASTM D4530	Standard Test Method for Determination of Carbon Residue (Micro Method)
ASTM D4715	Standard Test Method for Coking Value of Tar and Pitch (Alcan)
ASTM D4893	Standard Test Method for Determination of Pitch Volatility
ASTM D6560	Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products
ASTM E102	Standard Test Method for Saybolt Furol Viscosity of Bituminous Materials at High Temperatures

Annual Book of Standards. ASTM International, West Conshohocken, Pennsylvania.

Asphalt softens when heated and is elastic under certain conditions. The mechanical properties of asphalt are of particular significance when it is used as a binder or adhesive (Speight, 2014a, 2016, 2017). The principal application of asphalt is in road construction, which may be done in a variety of ways (Speight, 2014a, 2016), as well as, for example (as there are other uses), water-proofing for the roof of buildings and water-proofing for the foundations of building walls.

An asphalt emulsion is a mixture of asphalt and an anionic agent such as the sodium or potassium salt of a fatty acid. The fatty acid is usually a mixture and may contain palmitic, stearic, linoleic, and abietic acids and/or high molecular weight phenols. Sodium lignate (a product of the wood pulping industry) is often added to alkaline emulsions to effect better emulsion stability. Nonionic cellulose derivatives are also used to increase the viscosity of the emulsion if needed. The acid number of asphalt is an indicator of its emulsification capability and reflects the presence of high molecular weight asphaltogenic acids or naphthenic acids. Diamines, frequently used as cationic agents, are made from the reaction of tallow acid amines with acrylonitrile, followed by hydrogenation. The properties of

asphalt emulsions (ASTM D977, 2021; ASTM D2397, 2021) are adaptable to a variety of uses. As with other crude oil products, sampling is an important precursor to asphalt analysis and a standard method (ASTM D140, 2021) is available that provides guidance for the sampling of asphalt material (both liquid asphalt and semisolid asphalt) at point of manufacture, storage, or delivery.

Other important applications of asphalt include canal and reservoir linings, dam facings, and sea works. The asphalt so used may be a thin, sprayed membrane, covered with earth for protection against weathering and mechanical damage, or thicker surfaces, often including riprap (also known as rip rap, rip-rap, shot rock, rock armor, or rubble, is human-placed rock or other material used to protect shoreline structures against scour and water, wave, or ice erosion). Asphalt is also used for roofs, coatings, floor tiles, soundproofing, waterproofing, and other building-construction elements and in a number of industrial products, such as batteries. In some applications, an asphalt emulsion is used—in the emulsion, fine globules of the asphalt are suspended in water (Speight, 2014a, 2016).

When a residuum is obtained from a crude oil and thermal decomposition has commenced, it is more usual to refer to this product (typically a solid product) as “pitch.” Although there are occasions when refinery personally have referred to the non-cracked vacuum residuum as pitch or vacuum pitch.

The differences between a parent crude oil and the residua are due to the relative amounts of various constituents present, which are removed or remain by virtue of their relative volatility.

1.3.2.7 Tar and Pitch

Tar is a product of the destructive distillation of many bituminous substances or other organic materials and is a brown to black, oily, viscous liquid to semisolid material.

Tar is most commonly produced from bituminous coal and is generally understood to refer to the product from coal, although it is advisable to specify coal tar if there is the possibility of ambiguity (Speight, 2013a). Furthermore, an important (or key) factor in determining the yield and character of the coal tar is the carbonizing temperature. Three general temperature ranges are recognized, and the products have acquired the designations: low-temperature tar (approximately 450–700 °C; 540–1,290 °F), mid-temperature tar (approximately 700–900 °C; 1,290–1,650 °F), and high-temperature tar (approximately 900–1,200 °C; 1,650–2,190 °F). Tar released during the early stages of the decomposition of the organic material is called primary tar since it represents a product that has been recovered without the secondary alteration that results from prolonged residence of the vapor in the heated zone (Speight, 2013a).

Treatment of the distillate (boiling up to 250 °C, 480 °F) of the tar with caustic soda causes separation of a fraction known as tar acids; acid treatment of the

distillate produces a variety of organic nitrogen compounds known as tar bases. The residue left following removal of the high boiling material, or distillate, is typically referred to as pitch, which is a black, hard, and highly ductile material. In the chemical-process industries, pitch is the black or dark brown residue obtained by distilling coal tar, wood tar, fats, fatty acids, or fatty oils.

Coal tar pitch is typically a hard and brittle substance that typically contains aromatic resinous compounds along with aromatic and other hydrocarbons and their derivatives; it is used chiefly as road tar, in waterproofing roofs and other structures, and to make electrodes (Speight, 2013a). On the other hand, wood tar pitch is a bright, lustrous substance containing resin acids; it is used chiefly in the manufacture of a variety of products such as plastics, insulating materials, and caulking material. Pitch derived from fats, fatty acids, or fatty oils by distillation are usually soft substances containing polymers and decomposition products; they are used chiefly in varnishes and paints and in floor coverings.

Pitch lake is the name that has been applied to large surface deposit of bitumen. Guanoco Lake in Venezuela covers more than 1,100 acres and contains an estimated 35,000,000 bbl of bitumen. It was used as a commercial source of asphalt from 1891 to 1935. Smaller deposits occur commonly where Tertiary marine sediments outcrop on the surface; an example is the tar pits at Rancho La Brea in Los Angeles (brea and tar have been used synonymously with bitumen). Although most pitch lakes the remains of are formerly active seeps, some pitch lakes, such as the Pitch Lake on the island of Trinidad (covers 115 acres and contains an estimated 40,000,000 bbl of bitumen) continue to be supplied with fresh crude oil seeping from a subterranean source.

1.3.2.8 Sludge

In respect of completion of the potential viscous feedstocks, the material arbitrarily referred to as sludge should also be given some consideration.

Sludge can vary from a semisolid material to a solid material and can be generated from many of the refining processes, crude oil handling operations, as well as wastewater treatment (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). Sludge is often also referred to as a refinery waste and each component of the sludge can have its own impact on refinery operations as well as on the environment and there is always the potential for associated reactions between the sludge components that change the potential for the environmental impact—usually to a higher potential. Thus, knowledge of the composition of the sludge can be a necessary piece of information that will assist all aspects of the refinery operations. Application of the methods used to fractionate the viscous feedstocks may be applicable to defining the composition of the sludge into material that can be further refined or materials that are designated as refinery waste which should be disposed accordingly.

A significant portion of the sludge may be transported off-site and sold as by-products (Asia et al., 2006). These outputs include sulfur, acetic acid, phosphoric acid, and recovered metals. Metals from catalysts and from the crude oil that have deposited on the catalyst during the production often are recovered by third-party recovery facilities.

Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Finished crude oil products are also kept in storage tanks before transport off site. Storage tank bottoms are mixtures of sludge (typically emulsified oil and incompatible organic constituents as well as iron rust from corrosion) which accumulates at the bottom of tanks. Liquid tank bottoms are periodically drawn off to prevent their continued build up—sludge is also removed during periodic cleaning of tanks for inspection. Tank bottoms may contain amounts of tetraethyl or tetramethyl lead (although this is increasingly rare due to the phase-out of leaded products), other metals, and phenols.

Disposal of the sludge can be achieved by installation of a gasifier and, in fact, a wide variety of feedstocks can be considered for gasification, ranging from solids to liquids to gaseous streams. Although when the feed is a gas or liquid, the operation is frequently referred to as partial oxidation (POX). From a process perspective, partial oxidation of gases and liquids is very similar to the gasification of solids.

The major requirement for a suitable feedstock is that it contains a significant content of carbon and hydrogen. Solid feedstocks include solid waste, residua, visbreaker bottoms, crude oil coke, and even biomass—the streams most commonly employed are generally low-value by-products or waste streams generated by other processes (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017).

1.4 Classification

As already noted, the generic term heavy oil is often applied to crude oil that has an API gravity of less than 20° as well as those highly viscous naturally occurring materials (typically referred to as bitumen) having an API gravity less than 10° that have been referred to as bitumen (Speight, 2014a, 2015a). Considering the potential range of values from the standard test methods, the differentiation between an API gravity of 19.5° and 20.5° (for a top value of 20°) or 21.5° and 22.5° (for a top value of 22°) is difficult to determine as is the difference in the overall character of feedstocks having a viscosity of 9,500 and 10,500 cP.

Also, there has been an attempt to classify crude oil, heavy crude oil, and tar sand bitumen using the viscosity scale, and 10,000 cP being the fine line of demarcation between heavy oil and tar sand bitumen. Use of such a system leads to confusion when having to differentiate between a material having a viscosity of

9,950 cP and one having a viscosity of 10,050 cP as well as taking into account the limits of accuracy of the method of viscosity determination (Speight, 2014a, 2015a). Such definitions based on a single property should be discounted as being of little scientific value. Whether the limits are the usual laboratory experimental difference (typically $\pm 3\%$ of the acquired value by the relevant test method) or more likely the limits of accuracy of the method ($\pm 5\%$ to $\pm 10\%$), there is the question of viability and reliability of the definition. In fact, the limits of experimental difference of the method of measuring viscosity also increase the potential for misclassification using this (or any) single property for classification purposes.

Thus, in order to classify crude oil, heavy crude oil, and tar sand bitumen, the use of a single parameter such as API gravity or viscosity is not enough for classification purposes and any attempt to classify these feedstocks on the basis of a single property is no longer sufficient to define the nature and properties of crude oil and crude oil-related materials. The general classification method used for conventional crude oil, heavy crude oil, extra heavy crude oil, and tar sand bitumen involves not only an inspection of several properties but also some acknowledgment of the method of recovery.

Technically, heavy crude oil, extra heavy crude oil, and tar sand bitumen (relative to the more conventional crude oil fluids) have a high specific gravity, high viscosity, low atomic hydrogen-to-carbon (H/C) ratio as well as a high content of asphaltene constituents, resin constituents, sulfur, nitrogen, heavy metals and are often black in color (McCain, 1990; Meyer and De Witt, 1990; Meyer and Attanasi, 2003; Speight, 2014a).

Furthermore, to repeat and emphasize, one of the most appropriate means of classification of crude oil and the viscous feedstocks comes from the definition of tar sand bitumen offered by the United States Government for tar sands (Speight, 2014a, 2016):

Tar sands are the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques.

This definition allows a method by which refinery feedstocks can be categorized further reference to (1) the existence of the feedstock in the reservoir or deposit and (2) the method of (Table 1.8).

Heavy crude oil, extra heavy crude oil, and tar sand bitumen are all unconventional oil resources. The general classification of these feedstocks is related to the ease of flow of the material (Table 1.8) which indicates (1) the methods by which the material exits in the reservoir/deposit, (2) the methods of transportation, and (3) the methods of refining. Other pertinent properties used commercially are density and viscosity.

Other definitions (or attempted classification) of the viscous feedstocks are often based on the API gravity (which is a scale based on the oil relative density) as the criterion for classification. The API degree range that has been arbitrarily selected to define and classify refinery feedstocks oils has not been standardized. For example, the World Petroleum Conference has classified heavy crude oil as crude oil having an API gravity less than 22.3° API while the American Petroleum Institute suggests that heavy crude oil has an API gravity less and 20°. On the other hand, Petrobras suggests that heavy oil has an API gravity that falls in the range 10–19° API (Santos et al., 2014). There have also been attempts to classify crude oil and other refinery feedstocks on properties such as viscosity and sulfur content but classification based on a single property is fraught with errors and speculation.

Generally, heavy oil and tar bitumen are characterized by high viscosity (i.e., resistance to flow measured in centipoises or cP) and high density compared to conventional oil. Attempts have been made to define heavy oil as an oil with a gas-free viscosity between 100 and 10,000 cP at reservoir temperature (tar sand bitumen is incorrectly defined to have a viscosity greater than 10,000 cP, and may be as high as 10,000,000 cP). Attempting to draw a finite line in order to define heavy oil on the one side of the line and bitumen on the other side of the line is meaningless and incorrect and offers very little in the way of scientific integrity since the standard test methods that are used to determine viscosity suffer from reproducibility and accuracy (Speight, 2015a).

On the other hand, heavy oil is slightly less dense than water with a density on the order of 0.973 which represents an API gravity of 14° (water has a density of 1.00 which represents an API gravity of 10°). In addition, heavy oil can flow in some reservoirs at downhole temperatures that are above the pour point of the oil and/or with in situ solution gas, but at the surface, it is a thick, black, viscous fluid, which typically has an API gravity <10°. It should also be noted that the term oil sands as used in Canada was created for incentive tax purposes for those heavy crude oils found above a certain latitude where the infrastructure was almost nonexistent.

For correctness and to avoid confusion, the terms heavy oil, extra heavy oil, and bitumen should not be used interchangeably.

1.5 Feedstock Evaluation

The evaluation of any refinery feedstock involves application of a suite of analytical test methods and the data are used to determine the most appropriate processes to be employed in the refinery to convert the feedstock to a suite of useful products. As brief examples, the following properties are commonly applied (but are only a small selection of the analytical methods) to an evaluation of a refinery

feedstock: (1) density, which is used to assess the quality of the feedstock as well as in weight and volume conversion, (2) kinematic viscosity, which is an indicator of fluidity and is used in flow rate calculations and an indicator of fluid behavior, (3) pour point, which is the minimum temperature at which the feedstock will flow, (4) sulfur content which is used in quality control and feedstock evaluation, especially in terms of catalyst poisoning and equipment corrosion, and (5) component analysis, which is typically carried out by fractionation methods and the data are used to determine the processes that should be applied in the refinery.

Thus, the evaluation of refinery feedstocks is a necessary series of actions because of the variety of material that are accepted as feedstocks for the modern refinery. Also, the time when one crude oil as the sole feedstock for a refinery is limited (if not nonexistent) in the modern refinery because of the use of a blend of two or more crude oils as the refinery feedstock. Thus, evaluation of the blend (in fact, each of the components of the blend) is necessary to allow an assessment of the product slate and the processes that are necessary to create the saleable products. Thus, feedstock evaluation is the necessary application of a series of test methods in order to assess the chemical and physical properties of each of the constituents of the blend as well as the blend itself against a specific set of refinery-developed standards. A comprehensive feedstock evaluation is based on a detailed analysis necessary to determine the value of these crude oils to the refinery.

Accordingly, this section presents an outline of the tests that may be applied to crude oil, heavy crude oil, extra heavy crude oil, tar sand bitumen, and residua as well as biomass and their respective products as a pointer to the chemical properties and physical properties from which a feedstock or product can be evaluated.

The series of test methods are often referred to as the “feedstock assay” which consists of determination of (1) the feedstock assay, (2) the physical properties, (3) the thermal properties, (4) the chromatographic properties, and, when deemed appropriate, (5) the spectroscopic properties which offer insights into the chemical constituents in the feedstock and the potential for reaction of these chemical constituents with other constituents of the blend and with catalysts used in catalytic processes.

Thus, analyses are performed (by a series of standard test methods) to determine whether each batch of crude oil or the viscous feedstock received at the refinery is suitable not only for refining purposes but also to determine the preferential process options and the order in which the processes should be applied. To obtain the necessary information, two different analytical schemes are commonly used and these are: (1) an inspection assay and (2) a comprehensive assay (Table 1.15). The test applied to the feedstock to obtain the assay data are, for the purposes of this text, the standard methods as described by the ASTM International (formerly the American Society for Testing and Materials) (ASTM, 2021).

Table 1.15 Recommended Inspection Data Required for Crude Oil and the Viscous Feedstocks^a

Crude oil	Viscous feedstocks
Density, specific gravity	Density, specific gravity
API gravity	API gravity
Carbon (wt%)	Carbon (wt%)
Hydrogen (wt%)	Hydrogen (wt%)
Nitrogen (wt%)	Nitrogen (wt%)
Sulfur (wt%)	Sulfur (wt%)
	Nickel (ppm)
	Vanadium (ppm)
	Iron (ppm)
Pour point	Pour point
Wax content	
Wax appearance temperature	
Viscosity (various temperatures)	Viscosity (various temperatures)
Carbon residue of residuum	Carbon residue ^a
	Ash (wt%)
Distillation profile:	Fractional composition:
All fractions plus vacuum residue	Asphaltenes (% w/w)
	Resin constituents (% w/w)
	Aromatics (% w/w)
	Saturates (% w/w)

^a Includes heavy crude oil, extra heavy crude oil, tar sand bitumen, and residua.

An inspection assay (which is routinely performed on all feedstocks received at a refinery) typically involves determination of several bulk properties of the feedstock (such as API gravity, sulfur content, pour point, distillation range, viscosity, salt content, water and sediment content, and trace metals) as a means to determine if any major changes in characteristics have occurred since the last comprehensive assay was performed within the refinery. Other properties that are determined on an as needed basis include, but are not limited to, the following: (1) vapor pressure (Reid method) and the (2) total acid number. The results from these tests with the archived data from a comprehensive assay provide an estimate of any changes that have occurred in the crude oil that may be critical to refinery operations. The aforementioned inspection assay test methods are not

exhaustive but are the ones most commonly used and provide data on the impurities present as well as a general idea of the products that may be recoverable (Speight 2015a).

On the other hand, a full assay (also known as a comprehensive assay) is more complex and is usually performed when the feedstocks from a new field (in the case of crude oil and heavy crude oil) or a new deposit (in the case of extra heavy oil and tar sand bitumen) come onstream, or when the inspection assay indicates that significant changes in the composition of the feedstock have occurred. Except for these circumstances, a comprehensive assay of a particular feedstock may not (unfortunately) be updated for several years.

The data derived from the test assay can be used to assess the quality (and potential behavior) of the feedstock in the refinery and, therefore, indicate acquiring a degree of predictability of feedstocks performance during refining as well as the potential for changes to any material spilled into the environment. However, knowledge of the basic concepts of refining will help the analyst understand the production and, to a large extent, the anticipated properties of the product, which in turn is related to storage, sampling, and handling the products.

1.6 Modern Analytical Perspectives

The importance of chemical and physical properties is dependent upon the purity of the feedstock. In the strictest sense, refinery feedstocks are complex chemical mixtures which contain hydrocarbon derivatives and non-hydrocarbon derivatives that confer properties on the mixture that may not be reflected in the composition. Therefore, it is necessary to apply various standard test methods (as presented in the following chapters) to the feedstocks to determine if the material is suitable for processing and (in the case of the products) for sale with a designated use in mind. The more common tests are introduced in the following chapters and the test methods are presented in alphabetical order with no preference given to any particular test method.

Typically there are many standard test methods that have been developed for determining the properties of conventional crude oil and, therefore, some of these methods require modification for application to viscous refinery feedstocks while there is also the need to develop test methods that are particularly applicable to the viscous feedstocks not only as refinery feedstocks (or products) but also when the material is spilled into the environment. In fact, since the 1960s (especially after the so-called oil shocks of the 1970s) the development of viscous oil resources (particularly tar sand resources) became a major focus of many companies (Speight, 2013b, 2013c). These methods allowed refiners to have access to a literature database and to assess the capabilities and limitations of the application of

the analytical methods to the viscous feedstocks in order to accept these materials for refining as well as the identification of possible product slates.

However, before submitting a sample of a viscous feedstock for analysis, there is the need to ensure that the sample is representative. Typically, such methods also involve cleaning the sample by, for example, centrifugation and filtration, however, after dilution of the sample with a suitable (and easily removable) solvent, and the method should be acknowledged in a description of the method and the results (Wallace, 1988; Speight, 2015a). In addition, the viscous feedstocks typically contain substantial quantities of asphaltene constituents which not only may be a cause of instability and/or incompatibility but are also a precursor to coke formation as well as an indicator of the choice of upgrading options (Chapters 3 and 10) (Speight, 2015a, 2017).

More generally, and relative to conventional (light) crude oils, heavy crude oil, extra heavy crude oil, tar sand bitumen, and distillation residua are characterized by (1) low atomic H/C ratio; (2) high specific gravity; (3) high viscosity; (4) high contents of asphaltene constituents, resin constituents, and other constituents containing nitrogen, oxygen, sulfur, and heavy metals; and (5) often exhibit a near-black to black color (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017).

Analytical methods used to describe conventional oils must be modified for the characterization of the viscous feedstocks because of the variation in composition and properties of the viscous feedstocks when compared to conventional crude oil. For analytical properties that might be of minor importance in the conventional crude oil refining industry, there can be a quantum shift in importance of these same properties when used for refining the viscous feedstocks and there needs to be continued development of an acceptable analytical method that often begins with identification of the property that has to be determined.

As a result, research into methods for the measurement of properties of interest is ongoing in many laboratories that leads to the development of a variety of methods or modification of current methods. After this important step, there needs to be a reviewing process, deficiencies are identified, and promising methods are improved and acceptable.

In some cases, there have been questions about the application of methods developed for conventional crude oil to the viscous feedstocks. For example, (1) several methods are often available for the measurement of a given property but not all methods may be suitable for application to the viscous feedstocks, (2) some methods are more appropriate than others, (3) not all methods provide equivalent data, (4) different laboratories using the same method do not always report equivalent data for a given sample, and (5) in some analyses, the error in sampling and subsampling is greater than the error in the measurement.

Thus, a single standard method for conventional oil can therefore be the forerunner of several similar but distinct methods for a viscous feedstock. Moreover,

in order to meet the objective of accepting a new method of analysis, the following goals help the investigator (or the investigating organization) to meet this objective: (1) evaluation of existing methods by identifying the limitations and applicability of the method, (2) improvement of existing analytical methods, (3) development of new analytical methods, (4) standardization of analytical methods and adoption of recommended methods where applicable or desirable, and (5) development of recommended methods for sampling, sample storage, and sample preparation (Wallace, 1988).

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