1

PETROLEUM AND PETROLEUM PRODUCTS

1.1 INTRODUCTION

Petroleum (also called crude oil) is the term used to describe a wide variety of naturally occurring hydrocarbon-rich fluids that has accumulated in subterranean reservoirs and which exhibits considerably simple properties such as specific gravity/API gravity) and the amount of residuum (Table 1.1). More detailed inspections show considerable variations in color, odor, and flow properties that reflect the diversity of the origin of petroleum. From further inspections, variations also occur in the molecular types present in crude oil, which include compounds of nitrogen, oxygen, sulfur, metals (particularly nickel and vanadium), as well as other elements (ASTM D4175) (Speight, 2012a). Consequently, it is not surprising that petroleum can exhibit wide variations in refining behavior, product yields, and product properties (Speight, 2014a).

Over the past four decades, the petroleum being processed in refineries has become increasingly heavier (higher amounts of residuum) and higher sulfur content (Speight, 2000, 2014a; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007). Market demand (market pull) dictates that residua must be upgraded to higher-value products (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). In short, the value of petroleum depends upon its quality for refining and whether or not the product slate and product yields can be obtained to fit market demand.

Thus, process units in a refinery require analytical test methods that can adequately evaluate feedstocks and monitor product quality (Drews, 1998; Nadkarni, 2000, 2011; Rand, 2003; Totten, 2003). In addition, the high sulfur content of petroleum and regulations limiting the maximum sulfur content of fuels makes sulfur removal a priority in refinery processing. Here again, analytical methodology is key to the successful determination of the sulfur compound types present and their subsequent removal.

Upgrading residua involves processing (usually conversion) into a more salable, higher-valued product. Improved characterization methods are necessary for process design, crude oil evaluation, and operational control. Definition of the boiling range and the hydrocarbon-type distribution in heavy distillates and in residua is increasingly important. Feedstock analysis to provide a quantitative boiling range distribution (that accounts for non-eluting components) as well as the distribution of hydrocarbon types in gas oil and higher-boiling materials is important in evaluating feedstocks for further processing.

Sulfur reduction processes are sensitive to both amount and structure of the sulfur compounds being removed. Tests that can provide information about both are becoming increasingly important, and analytical tests that provide information about other constituents of interest (e.g., nitrogen, organometallic constituents) are also valuable and being used for characterization.

But before emerging into the detailed aspects of petroleum product analysis, it is necessary to understand the nature of petroleum as well as the refinery processes required to produce petroleum products. This will present to the reader the background that is necessary to understand petroleum and the processes used to convert it to products. The details of the chemistry are not presented here and can be found elsewhere (Speight, 2000, 2014a; Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007).
TABLE 1.1 Illustration of the variation in petroleum properties—specific gravity/API gravity) and the amount of residuum

<table>
<thead>
<tr>
<th>Petroleum</th>
<th>Specific gravity</th>
<th>API gravity</th>
<th>Residuum &gt;1050°F (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agbami (Africa)</td>
<td>0.790</td>
<td>48.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Alaska North Slope (US)</td>
<td>0.869</td>
<td>31.4</td>
<td>18.3</td>
</tr>
<tr>
<td>Alba (North Sea)</td>
<td>0.936</td>
<td>19.5</td>
<td>32.7</td>
</tr>
<tr>
<td>Alvheim Blend (North Sea)</td>
<td>0.850</td>
<td>34.9</td>
<td>13.1</td>
</tr>
<tr>
<td>Azeri BTC (Asia)</td>
<td>0.843</td>
<td>36.4</td>
<td>13.2</td>
</tr>
<tr>
<td>Badak (Indonesia)</td>
<td>0.830</td>
<td>38.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Bahrain (Bahrain)</td>
<td>0.861</td>
<td>32.8</td>
<td>26.4</td>
</tr>
<tr>
<td>California (US)</td>
<td>0.858</td>
<td>33.4</td>
<td>23.0</td>
</tr>
<tr>
<td>Calypso (Trinidad and Tobago)</td>
<td>0.971</td>
<td>30.8</td>
<td>11.6</td>
</tr>
<tr>
<td>Dalix (Africa)</td>
<td>0.915</td>
<td>23.1</td>
<td>27.7</td>
</tr>
<tr>
<td>Dansk Underground Consortium (DUC) (Denmark)</td>
<td>0.860</td>
<td>33.5</td>
<td>18.2</td>
</tr>
<tr>
<td>Draugen (Europe)</td>
<td>0.826</td>
<td>39.9</td>
<td>6.4</td>
</tr>
<tr>
<td>Gimboa (Africa)</td>
<td>0.912</td>
<td>25.3</td>
<td>24.0</td>
</tr>
<tr>
<td>Grane (North Sea)</td>
<td>0.940</td>
<td>19.0</td>
<td>30.3</td>
</tr>
<tr>
<td>Hibernia Blend (Canada)</td>
<td>0.850</td>
<td>35.0</td>
<td>17.2</td>
</tr>
<tr>
<td>Iranian Light (Iran)</td>
<td>0.836</td>
<td>37.8</td>
<td>20.8</td>
</tr>
<tr>
<td>Iraq Light (Iraq)</td>
<td>0.844</td>
<td>36.2</td>
<td>23.8</td>
</tr>
<tr>
<td>Kearn (Canada)</td>
<td>0.918</td>
<td>22.6</td>
<td>31.9</td>
</tr>
<tr>
<td>Kutubu Bland (New Guinea)</td>
<td>0.802</td>
<td>44.8</td>
<td>12.0</td>
</tr>
<tr>
<td>Kuwaiti Light (Kuwait)</td>
<td>0.860</td>
<td>33.0</td>
<td>31.9</td>
</tr>
<tr>
<td>Marib Light (Yemen)</td>
<td>0.809</td>
<td>43.3</td>
<td>7.7</td>
</tr>
<tr>
<td>Medanito (Argentina)</td>
<td>0.860</td>
<td>33.0</td>
<td>20.6</td>
</tr>
<tr>
<td>Mondo (Africa)</td>
<td>0.877</td>
<td>29.9</td>
<td>22.1</td>
</tr>
<tr>
<td>Oklahoma (US)</td>
<td>0.816</td>
<td>41.9</td>
<td>20.0</td>
</tr>
<tr>
<td>Oman (Oman)</td>
<td>0.873</td>
<td>30.5</td>
<td>30.5</td>
</tr>
<tr>
<td>Pennsylvania (US)</td>
<td>0.800</td>
<td>45.4</td>
<td>2.0</td>
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<td>Peregrino (Brazil)</td>
<td>0.974</td>
<td>13.7</td>
<td>40.5</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>0.840</td>
<td>37.0</td>
<td>27.5</td>
</tr>
<tr>
<td>Saxi Batque Blend (Africa)</td>
<td>0.856</td>
<td>33.9</td>
<td>14.6</td>
</tr>
<tr>
<td>Terra Nova (Canada)</td>
<td>0.859</td>
<td>0.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Texas (US)</td>
<td>0.827</td>
<td>39.6</td>
<td>15.0</td>
</tr>
<tr>
<td>Texas (US)</td>
<td>0.864</td>
<td>32.3</td>
<td>27.9</td>
</tr>
<tr>
<td>Venezuela</td>
<td>0.950</td>
<td>17.4</td>
<td>33.6</td>
</tr>
<tr>
<td>Zakhum Lower (Abu Dhabi)</td>
<td>0.822</td>
<td>40.5</td>
<td>14.3</td>
</tr>
</tbody>
</table>

1.2 PERSPECTIVES

The following sections are included to introduce the reader to the distant historical and recent historical aspects of petroleum analysis and to show the glimmerings of how it has evolved during the twentieth century and into the twenty-first century. Indeed, in spite of the historical use of petroleum and related materials, the petroleum industry is a modern industry having come into being in 1859. From these comparatively recent beginnings, petroleum analysis has arisen as a dedicated science.

1.2.1 Historical Perspectives

Petroleum is perhaps the most important substance consumed in modern society. The word petroleum, derived from the Latin petra and oleum, means literally rock oil and refers to hydrocarbons that occur widely in the sedimentary rocks in the form of gases, liquids, semisolids, or solids. Petroleum provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation.

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 petroleum, petroleum derivatives (naphtha), heavy oil, and bitumen are not new. The use of petroleum and its derivatives was practiced in pre-Christian times and is known largely through historical use in many of the older civilizations (Henry, 1873; Abraham, 1945; Forbes, 1958a, 1958b, 1959, 1964; James and Thorpe, 1994). Thus, the use of petroleum and the development of related technology are not such a modern subject as we are inclined to believe. However, the petroleum industry is essentially a twentieth-century
industry, but to understand the evolution of the industry, it is essential to have a brief understanding of the first uses of petroleum.

Briefly, petroleum and bitumen have been used for millennia. For example, 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 zigzurats, had an impressive law, as well as a wide and varied collection of literature. As the culture developed, bitumen (sometimes referred to as natural-occurring asphalt) was frequently used in construction and in ornamental works. Although it is possible, on this basis, to differentiate between the words bitumen and asphalt in modern use (Speight, 2014a), the occurrence of these words in older texts offers no such possibility. It is significant that the early use of bitumen was in the nature of cement for securing or joining together various objects, and it thus seems likely that the name itself was expressive of this application.

Early references to petroleum and its derivatives occur in the Bible, although by the time the various books of the Bible were written, the use of petroleum and bitumen was established. Investigations at historic sites have confirmed the use of petroleum and bitumen in antiquity for construction, mummification, decorative jewelry, waterproofing, as well as for medicinal use (Speight, 2014a). Many other references to bitumen occur throughout the Greek and Roman empires, and from then to the Middle Ages, early scientists (alchemists) frequently referred to the use of bitumen. In the late fifteenth and early sixteenth centuries, both Christopher Columbus and Sir Walter Raleigh have been credited with the discovery of the asphalt deposit on the island of Trinidad and apparently used the material to caulk their ships. There was also an interest in the thermal product of petroleum (nafta; naphtha) when it was discovered that this material could be used as an illuminant and as a supplement to asphalt incendiaries in warfare.

To continue such references is beyond the scope of this book, although they do give a flavor of the developing interest in petroleum. However, it is sufficient to note that there are many other references to the occurrence and use of bitumen or petroleum derivatives up to the beginning of the modern petroleum industry (Speight, 2014a). However, what is obvious by its absence is any reference to the analysis of the bitumen that was used variously through history. It can only be assumed that there was a correlation between the bitumen character and its behavior. This would be the determining factor(s) in its use as a sealant, a binder, or as a medicine. In this sense, documented history has not been kind to the scientist or engineer.

Thus, the history of analysis of petroleum and its products (as recognized by the modern scientist and engineer) can only be suggested to have started during the second half of the nineteenth century. Further developments of the analytical chemistry of petroleum continued throughout the twentieth century, and it is only through chemical and physical analysis that petroleum can be dealt with logically.

1.2.2 Modern Perspectives

The modern petroleum industry began in 1859 with the discovery and subsequent commercialization of petroleum in Pennsylvania (Speight, 2014a). During the 6000 years of its use, the importance of petroleum 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 (Speight, 2014a). However, what is more pertinent to the industry is that throughout the millennia in which petroleum has been known and used, it is only in the twentieth century that attempts have been made to formulate and standardize petroleum analysis.

As the twentieth century matured, there was increased emphasis and reliance on instrumental approaches to petroleum analysis. In particular, spectroscopic methods have risen to a level of importance that is perhaps the dreams of those who first applied such methodology to petroleum analysis. There are also potentiometric titration methods that evolved, and the procedures have found favor in the identification of functional types in petroleum and its fractions.

Spectrophotometers came into widespread use—approximately beginning in 1940—and this led to wide acquisition in petroleum analysis (Chapter 2). Ultraviolet absorption spectroscopy, infrared spectroscopy, mass spectrometry, emission spectroscopy, and nuclear magnetic resonance spectroscopy continue to make major contributions to petroleum analysis (Nadkarni, 2011; Totten, 2003).

Chromatography is another method that is utilized for the most part in the separation of complex mixtures and has found wide use in petroleum analysis (Chapter 2). Ion exchange materials, long known in the form of naturally occurring silicates, were used in the earliest types of regenerable water softeners. Gas chromatography, or vapor-phase chromatography, found ready applications in the identification of the individual constituents of petroleum. It is still extremely valuable in the analysis of hydrocarbon mixtures of high volatility and has become an important analytical tool in the petroleum industry. With the development of high-temperature columns, the technique has been extended to mixtures of low volatility, such as gas oils and some residua.

In fact, in the petroleum refining industry, boiling range distribution data (for example ASTM D3710) are used (i) to assess petroleum crude quality before purchase, (ii) to monitor petroleum quality during transportation, (iii) to evaluate petroleum for refining, and (iv) to provide information for the optimization of refinery processes. Traditionally, boiling
range distributions of the various fractions have been determined by distillation. Yield-on-crude data are still widely reported in the petroleum assay literature, providing information on the yield of specific fractions obtained by distillation (ASTM D86, ASTM D1160). However, to some extent in the laboratory, atmospheric and vacuum distillation techniques have largely been replaced by simulated distillation methods, which use low-resolution gas chromatography and correlate retention times to hydrocarbon boiling points (ASTM D2887, ASTM), which typically use external standards such as n-alkanes.

1.3 DEFINITIONS

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

For the purposes of this book, petroleum products and those products that are isolated from petroleum during recovery (such as natural gas, natural gas liquids, and natural gasoline) as well as refined products—petrochemical products—are excluded from this text.

Furthermore, it is necessary to state for the purposes of this text that on the basis of being chemically correct, it must be recognized that hydrocarbon molecules (hydrocarbon oils) contain carbon atoms and hydrogen atoms only. The presence of atoms (such as nitrogen, oxygen, sulfur, and metals) other than carbon and hydrogen leads to the definition and characterization of such materials as hydrocarbonaceous oils. Also, for the purposes of terminology, it is often convenient to subdivide petroleum and related materials into three major groups (Table 1.2) (Speight, 2014a): (i) materials that are of natural origin, (ii) materials that are manufactured, and (iii) materials that are integral fractions derived from the natural or manufactured products (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

1.3.1 Petroleum

Petroleum 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) (Speight, 2000, 2014a). Although petroleum and fractions thereof have been known since ancient time (Henry, 1873; Abraham, 1945; Forbes, 1958a, b, 1959, 1964; James and Thorpe, 1994; Speight, 2014a),

<table>
<thead>
<tr>
<th>Table 1.2 Subdivision of fossil fuels into various subgroups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Materials</td>
</tr>
<tr>
<td>Natural gas</td>
</tr>
<tr>
<td>Petroleum</td>
</tr>
<tr>
<td>Heavy oil</td>
</tr>
<tr>
<td>Bitumen*</td>
</tr>
<tr>
<td>Asphaltite</td>
</tr>
<tr>
<td>Asphaltoid</td>
</tr>
<tr>
<td>Ozocerite (natural wax)</td>
</tr>
</tbody>
</table>

*Bitumen from tar sand deposits.
¹Products of petroleum processing.

the current era of petroleum and petroleum product analysis might be assigned to commence in the early-to-mid nineteenth century (Silliman, Sr., 1833. Silliman, Jr., 1860, 1865, 1867, 1871) and continued thereafter. Historically, physical properties such as boiling point, density (gravity), odor, and viscosity have been used to describe crude oil (Speight, 2014a). Petroleum may be called light or heavy in reference to the amount of low-boiling constituents and the relative density (specific gravity). Likewise, odor is used to distinguish between sweet (low-sulfur) and sour (high-sulfur) crude oil. Viscosity indicates the ease of (or more correctly the resistance to) flow.

Briefly, the measurement of density is not a pro-forma (i.e., nice-to-have) piece of data as it is often used in combination with other test results to predict crude oil quality. Density or relative density (specific gravity) is used whenever conversions must be made between mass (weight) and volume measurements. Various ASTM procedures for measuring density or specific gravity are also generally applicable to heavy (viscous) oil. In the test methods, heavy oils generally do not create problems because of sample volatility, but the test methods are sensitive to the presence of gas bubbles in the heavy oil, and particular care must be taken to exclude or remove gas bubbles before measurement. In addition, heavy oils (with the exception of the more viscous petroleum products such as lubricating oil and white oil) are typically dark-colored samples, and it may be difficult to ascertain whether or not all air bubbles have been eliminated from the sample.

However, there is the need for a thorough understanding of petroleum and the associated technologies; it is essential that the definitions and the terminology of petroleum science and technology be given prime consideration (Speight, 2014a). This presents a better understanding of petroleum, 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. This part of the text attempts to alleviate much of the confusion that exists, but it must be remembered that the terminology of petroleum is still open to personal choice and historical usage.

Conventional (light) petroleum is composed of hydrocarbons together with smaller amounts of organic compounds of nitrogen, oxygen, and sulfur and still smaller amounts of compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper. The processes by which petroleum was formed dictate that petroleum composition will vary and be site specific thus leading to a wide variety of compositional differences. By using the term site specific, it is intended to convey that petroleum composition will be dependent upon regional and local variations in the proportion of the various precursors that went into the formation of the protopetroleum as well as variations in temperature and pressure to which the precursors were subjected.

The active principle is that petroleum is a continuum and has natural product origins (Speight, 2014a). As such, it might be anticipated that there is a continuum of different molecular systems throughout petroleum that might differ from volatile to nonvolatile fractions but which, in fact, are based on natural product systems. It might also be argued that substitution patterns on the aromatic nucleus that are identified in the volatile fractions, or in any natural product counterparts, may also apply to the substitution patterns on the aromatic nucleus of aromatic systems in the nonvolatile fractions.

Because of the complexity of the precursor mix that leads to the intermediate that is often referred to as protopetroleum and which eventually to petroleum, the end product contains an extreme range of organic functionality and molecular size. In fact, the large variety of the molecular constituents of petroleum makes it unlikely that a complete compound-by-compound description for even a single crude oil would be possible. Those who propose such molecular identification projects may be in for a very substantial surprise, especially when dealing with heavy oil, extra heavy oil, and tar sand bitumen. At the same time, it must be wondered how such a project, if successful, will help the refiner.

On the other hand, the molecular composition of petroleum can be described in terms of three classes of compounds: saturates, aromatics, and compounds bearing heteroatoms (nitrogen, oxygen, sulfur, and/or metals). Within each class, there are several families of related compounds. The distribution and characteristics of these molecular species account for the rich variety of crude oils. This is the type of information with some modification, but without the need for full molecular identification, that refiners have used for decades with considerable success.

There is no doubt of the need for the application of analytical techniques to petroleum-related issues—refining and environmental—and, accordingly, interest in petroleum analysis has increased over the past four decades because of the change in feedstock composition and feedstock type because of the higher demand for liquid fuels and the increased amounts of the heavier feedstocks that are now used as blendstocks in many refineries. Prior to the energy crises of the 1970s, the heavier feedstocks were used infrequently as sources of liquid fuels and were used to produce asphalt, but, now, these feedstocks have increased in value as sources of liquid fuels.

In conventional (light, sweet) petroleum, the content of pure hydrocarbons (i.e., molecules composed of carbon and hydrogen only) may be as high as 80% w/w for paraffinic petroleum and less than 50% w/w for heavy crude oil and much lower for tar sand bitumen. The non-hydrocarbon constituents are usually concentrated in the higher-boiling portions of the crude oil. The carbon and hydrogen contents are approximately constant from crude oil to crude oil even though the amounts of the various hydrocarbon types and of the individual isomers may vary widely. Thus, the carbon content of various types of petroleum is usually between 83 and 87% by weight, and the hydrogen content is in the range of 11–14% by weight.

The near-constancy of carbon content and the hydrogen content is explained by the fact that variation in the amounts of each series of hydrocarbons does not have a profound effect on overall composition (Speight, 2014a). However, within any petroleum or heavy oil, the atomic ratio of hydrogen to carbon increases from the low-to the high-molecular-weight fractions. This is attributable to an increase in the content of polynuclear aromatics and multi-ring cycloparaffins that are molecular constituents of the higher-boiling fractions. For higher-boiling feedstocks such as heavy oil and bitumen, the chemical composition becomes so complex and its relationship to performance so difficult to define that direct correlation of atomic ratios is not always straightforward. In any case, simpler tests are required for quality control purposes. Analysis is typically confined to the determination of certain important elements and to the characterization of the feedstock in terms of a variety of structural groups that have the potential to interfere with the thermal decomposition and also with catalysts. Thus, for heavy oil, bitumen, and residua, density and viscosity still are of great interest. But for such materials, hydrogen, nitrogen, sulfur, and metal content as well as carbon residue values become even more important (Table 1.1).

General aspects of petroleum quality (as a refinery feedstock) are assessed by the measurement of physical properties such as relative density (specific gravity), refractive index, or viscosity, or by empirical tests such as pour point or oxidation stability that are intended to relate to behavior in service. In some cases, the evaluation may include tests in
mechanical rigs and engines either in the laboratory or under actual refinery process conditions.

In the crude state, petroleum has minimal value, but when refined, it provides high-value liquid fuels, solvents, lubricants, and many other products (Speight, 2014a and references cited therein). The fuels derived from petroleum 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. Petroleum 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 petroleum is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). And the terminology of these fractions has been bound by utility and often bears little relationship to composition.

The molecular boundaries of petroleum cover a wide range of boiling points and carbon numbers of hydrocarbon compounds and other compounds containing nitrogen, oxygen, and sulfur, as well as metallic (porphyrin) constituents. However, the actual boundaries of such a petroleum map can only be arbitrarily defined in terms of boiling point and carbon number (Fig. 1.1). In fact, petroleum is so diverse that materials from different sources exhibit different boundary limits, and for this reason—more than for any other reason—it is not surprising that petroleum has been difficult to map in a precise manner (Speight, 2014a).

Since there is a wide variation in the properties of crude petroleum, the proportions in which the different constituents occur vary with origin (Speight, 2014a). Thus, some crude oils have higher proportions of the lower-boiling components and others (such as heavy oil and bitumen) have higher proportions of higher-boiling components (asphaltic components and residuum).

There are several other definitions that also need to be included in any text on petroleum analysis, in particular since this text also focuses on the analysis of heavy oil and bitumen. These definitions are included because of the increased reliance on the development of these resources and the appearance of the materials in refineries.

Because of the wide range of chemical and physical properties, a wide range of tests have been (and continue to be) developed to provide an indication of the means by which a particular feedstock should be processed. Initial inspection of the nature of the petroleum will provide deductions about the most logical means of refining or correlation of various properties to structural types present and hence attempted classification of the petroleum. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of their significance.

In terms of the definition of petroleum, there are two formulas that can serve to further defining petroleum and its products: (i) the correlation index and (ii) the characterization factor—both of which are a means of estimating the character and behavior of crude oil. Both methods rely upon various analytical methods to derive data upon which the outcomes are based.

### 1.3.1.1 Correlation Index

The correlation index is based on the plot of specific gravity versus the reciprocal of the boiling point in degrees Kelvin ($^\circ K=^\circ C+273$). For pure hydrocarbons, the line described by the constants of the individual members of the normal paraffin series is given a value of CI=0 and a parallel line passing through the point for the values of benzene is given as CI=100; thus,

$$CI = 473.7d - 456.8 + 48,640/K$$

In this equation, $d$ is the specific gravity and $K$ is the average boiling point of the petroleum fraction as determined by the standard distillation method.

Values for the index between 0 and 15 indicate a predominance of paraffinic hydrocarbons in the fraction. A value from 15 to 50 indicates predominance of either naphthenes or of mixtures of paraffins, naphthenes, and aromatics. An index value above 50 indicates a predominance of aromatic species. However, it cannot be forgotten that the data used to determine the correlation index are average for the fraction of feedstock under study and may not truly represent all
constituents of the feedstock, especially those at both ends of a range of physical and chemical properties.

Thus, because of the use of average data and the output of a value that falls within a broad range, it is questionable whether or not this correlation index offers realistic or reliable information. As the complexity of feedstocks increase from petroleum to heavy oil and beyond to tar sand bitumen, especially with the considerable overlap of compound types, there must be serious questions about the reliability of the number derived by this method.

1.3.1.2 Characterization Factor
Another derived number, the characterization factor (sometime referred to as the UOP characterization factor or the Watson characterization factor), is also a widely used method for defining petroleum, and it is derived from the following formula, which is a relationship between boiling point and specific gravity:

\[ K = \frac{\sqrt{T_k}}{d} \]

In this equation, \( T_k \) is the average boiling point in degrees Rankine (°F+460), and \( d \) is the specific gravity (60°/60°F). This factor has been shown to be additive on a weight basis. It was originally devised to show the thermal cracking characteristics of heavy oil. Thus, highly paraffinic oils have \( K \approx \) ca. 12.5–13.0, and cyclic (naphthenic) oils have \( K \approx \) ca. 10.5–12.5.

Again, because of the use of average data and the output of a value that falls (in this case) within a narrow range, it is questionable whether or not the data offer realistic or reliable information. Determining whether or not a feedstock is paraffinic is one issue, but one must ask if there is a real difference between feedstocks when the characterization factor is 12.4 or 12.5 or even between feedstocks having characterization factors of 12.4 and 13.0. As the complexity of feedstocks increases from petroleum to heavy oil and beyond to extra heavy oil and tar sand bitumen, especially with the considerable overlap of compound types, there must be serious questions about the reliability of the number derived by this method.

1.3.1.3 Character and Behavior
The data derived from any one or more of the analytical techniques give an indication of the characteristics of petroleum and an indication of the methods of feedstock processing as well as for the predictability of product yields and properties (Dolbear et al., 1987; Speight, 2000, 2014a and references cited therein).

The most promising means of predictability of feedstock behavior during processing and predictability of product yields and properties have arisen from the concept of feedstock mapping (Long and Speight, 1998; Speight, 2014a). In such procedures, properties of feedstock are mapped to show characteristics that are in visual form rather than in tabular form. In this manner, the visual characteristics of the feedstock are used to evaluate and predict the behavior of the feedstock in various refining scenarios. Whether or not such methods will replace the simpler form of property correlations remains to be determined. It is more than likely that both will continue to be used in a complimentary fashion for some time to come. However, there is also the need to recognize that what is adequate for one refinery and one feedstock (or feedstock blend provided that the blend composition does not change significantly) will not be suitable for a different refinery with a different feedstock (or feedstock blend).

One of the most effective means of feedstock mapping has arisen through the use of a multidisciplinary approach that involves use of all of the necessary properties of a feedstock. However, it must be recognized that such maps do not give any indication of the complex interactions that occur between, for example, such fractions as the asphaltene constituents and resins as well as the chemical transformations and interactions that occur during processing (Koots and Speight, 1975; Speight, 1994, Ancheyta et al., 2010), but it does allow predictions of feedstock behavior. It must also be recognized that such a representation varies for different feedstocks. More recent work related to feedstock mapping has involved the development of a different type of compositional map using the molecular weight distribution and the molecular type distribution as coordinates. Such a map can provide insights into many separation and conversion processes used in petroleum refining (Long and Speight, 1998; Speight, 2014a).

Thus, a feedstock map can be used to show where a particular physical or chemical property tends to concentrate on the map. For example, the coke-forming propensity, that is, the amount of the carbon residue, can be illustrated for various regions on the map for a sample of atmospheric residuum (Long and Speight, 1998; Speight, 2014a). In addition, a feedstock map can be extremely useful for predicting the effectiveness of various types of separation (and other refinery) processes as applied to petroleum (Long and Speight, 1998; Speight, 2014a).

In contrast to the cut lines generated by separation processes, conversion processes move materials in the composition from one molecular type to another. For example, reforming converts saturates to aromatics and hydrogenation converts aromatic molecules to saturated molecules and polar aromatic molecules to either aromatic molecules or saturated molecules (Speight, 2014a). Hydrotreating removes nitrogen and sulfur compounds from polar aromatics without much change in molecular weight, while hydrocracking converts polar species to aromatics while at the same time reducing molecular weight. Visbreaking and heat soaking primarily lower or raise the molecular weight of the polar species in the composition map. Thus, visbreaking is used to
lower the viscosity of heavy oils, whereas heat soaking is a
cooking method. Thus, conversion processes can change the
shape and size of the composition map.

Thus, the data derived from any one, or more, of the analy-
tical methods described in this chapter can be combined to
give an indication of the characteristics of the feedstock as
well as options for feedstock processing as well as for the
prediction of product properties. Indeed, the use of physical
properties for feedstock evaluation has continued in refin-
eries and in process research laboratories to the present time
and will continue for some time. It is, of course, a matter of
choosing the relevant and meaningful properties to meet the
nature of the task. What is certain is that the use of one single
property cannot accurately portray the character and behavior
of petroleum.

1.3.1.4 Bulk Fractions
While not truly a petroleum product in the refining sense, the
bulk fractions produced from petroleum during laboratory
fractionation studies can also be designated as derived mate-
rials and, thence, petroleum products. The data derived from
the analysis of these fractions can be used to predict the refin-
ability of the crude oil and to formulate refining procedures.

Briefly, in addition to distillation, petroleum can be sub-
divided into bulk fractions by a variety of precipitation/
adsorption procedures: (i) asphaltene constituents, (ii) resin
constituents, (iii) aromatic constituents, and (iv) saturated
constituents (Fig. 1.2) (Speight, 2014a). However, the frac-
tionation methods available to the petroleum industry allow
a reasonably effective degree of separation of hydrocarbon
mixtures. However, the problems are separating the petroleum
constituents without alteration of their molecular structure
and obtaining these constituents in a substantially pure state.
Thus, the general procedure is to employ techniques that
segregate the constituents according to molecular size and
molecular type. Furthermore, the names given to the fraction
(i.e., asphaltene constituents, resin constituents, aromatic
constituents, and saturated constituents) are based on separa-
tion procedures rather than on an accurate account of the
molecular constituents of the fractions.

These investigations of the character of petroleum have
been focused on the influence of the bulk makeup of petro-
leum on refining operations and the nature of the products
that will be produced. However, the fractional composition
of petroleum varies markedly with the method of isolation or
separation, thereby leading to potential complications (espe-
cially in the case of the heavier feedstocks) in the choice of
suitable processing schemes for these feedstocks. Because
of this, the application of analytical techniques to these
other petroleum products should also be applied assiduously
and the data interpreted accordingly.

1.3.2 Natural Gas

Natural gas is the gaseous mixture associated with petro-
leum reservoirs and is predominantly methane, but does con-
tain other combustible hydrocarbon compounds as well as
non-hydrocarbon compounds (Mokhatab et al., 2006,
Speight 2014a). In fact, associated natural gas is believed to
be the most economical form of ethane.

The gas occurs in the porous rock of the earth’s crust
either alone or with accumulations of petroleum. In the latter

**FIGURE 1.2** Feedstock fractionation.
case, the gas forms the gas cap, which is the mass of gas trapped between the liquid petroleum and the impervious cap rock of the petroleum reservoir. When the pressure in the reservoir is sufficiently high, the natural gas may be dissolved in the petroleum and is released upon penetration of the reservoir as a result of drilling operations.

Natural gas is also associated with shale formations, and such gas is commonly referred to as shale gas—to define the origin of the gas rather than the character and properties (Speight, 2013b). Chemically, shale gas is typically a dry gas composed primarily of methane (60–95% v/v), but some formations do produce wet gas—in the United States, the Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development. Analysis of shale gas follows the methods of analysis for natural gas.

The principal types of gaseous fuels are oil (distillation) gas, reformed natural gas, and reformed propane or liquefied petroleum gas (LPG). Mixed gas is a gas prepared by adding natural gas or LPG to a manufactured gas, giving a product of better utility and higher heat content or Btu value.

The principal constituent of natural gas is methane (CH4). Other constituents are paraffinic hydrocarbons such as ethane (CH3CH3), propane, and the butanes. Many natural gases contain nitrogen (N2) as well as carbon dioxide (CO2) and hydrogen sulfide (H2S). Trace quantities of argon, hydrogen, and helium may also be present. Generally, the hydrocarbons having a higher molecular weight than methane, carbon dioxide, and hydrogen sulfide are removed from natural gas prior to its use as a fuel. Gases produced in a refinery contain methane, ethane, ethylene, propylene, hydrogen, carbon monoxide, carbon dioxide, and nitrogen, with low concentrations of water vapor, oxygen, and other gases.

Types of natural gas vary according to composition. There is dry gas or lean gas, which is mostly methane, and wet gas, which contains considerable amounts of higher-molecular-weight and higher-boiling hydrocarbons (Mokhatab et al., 2006; Speight, 2007, 2014a). Sour gas contains high proportions of hydrogen sulfide, whereas sweet gas contains little or no hydrogen sulfide. Residue gas is the gas remaining (mostly methane) after the higher-molecular-weight paraffins has been extracted. Casinghead gas is the gas derived from an oil well by extraction at the surface. Natural gas has no distinct odor and the main use is for fuel, but it can also be used to make chemicals and LPG.

Some natural gas wells also produce helium, which can occur in commercial quantities; nitrogen and carbon dioxide are also found in some natural gases. Gas is usually separated at as high a pressure as possible, reducing compression costs when the gas is to be used for gas lift or delivered to a pipeline. After gas removal, lighter hydrocarbons and hydrogen sulfide are removed as necessary to obtain petroleum of suitable vapor pressure for transport yet retaining most of the natural gasoline constituents.

In addition to composition and thermal content (Btu/scf, Btu/ft3), natural gas can also be characterized on the basis of the mode of the natural gas found in reservoirs where there is no, or at best only minimal amounts of, petroleum.

Thus, there is nonassociated natural gas, which is found in reservoirs in which there is no, or at best only minimal amounts of, petroleum. Nonassociated gas is usually richer in methane but is markedly leaner in terms of the higher-molecular-weight hydrocarbons and condensate. Conversely, there is also associated natural gas (dissolved natural gas) that occurs either as free gas or as gas in solution in the petroleum. Gas that occurs as a solution with the crude petroleum is dissolved gas, whereas the gas that exists in contact with the crude petroleum (gas cap) is associated gas. Associated gas is usually leaner in methane than the nonassociated gas but is richer in the higher-molecular-weight constituents.

The most preferred type of natural gas is the nonassociated gas. Such gas can be produced at high pressure, whereas associated, or dissolved, gas must be separated from petroleum at lower separator pressures, which usually involves increased expenditure for compression. Thus, it is not surprising that such gas (under conditions that are not economically favorable) is often flared or vented.

As with petroleum, natural gas from different wells varies widely in composition and analyses (Mokhatab et al., 2006; Speight, 2014a and references cited therein), and the proportion of non-hydrocarbon constituents can vary over a very wide range. The non-hydrocarbon constituents of natural gas can be classified as two types of materials: (i) diluents, such as nitrogen, carbon dioxide, and water vapors; and (ii) contaminants, such as hydrogen sulfide and/or other sulfur compounds. Thus, a particular natural gas field could require production, processing, and handling protocols different from those used for gas from another field.

The diluents are noncombustible gases that reduce the heating value of the gas and are on occasion used as fillers when it is necessary to reduce the heat content of the gas. On the other hand, the contaminants are detrimental to production and transportation equipment in addition to being obnoxious pollutants. Thus, the primary reason for gas refining is to remove the unwanted constituents of natural gas and to separate the gas into its various constituents. The processes are analogous to the distillation unit in a refinery where the feedstock is separated into its various constituent fractions before further processing to products.

The major diluents or contaminants of natural gas are (i) acid gas, which is predominantly hydrogen sulfide although carbon dioxide does occur to a lesser extent; (ii) water, which includes all entrained free water or water in condensed forms; (iii) liquids in the gas, such as
higher-boiling hydrocarbons as well as pump lubricating oil, scrubber oil, and, on occasion, methanol; and (iv) any solid matter that may be present, such as fine silica (sand) and scaling from the pipe.

1.3.3 Natural Gas Liquids and Natural Gasoline

Natural gas liquids are products other than methane from natural gas: ethane, butane, iso-butane, and propane. Natural gasoline may also be included in this group.

Natural gas liquids are, in fact, separate and distinct hydrocarbons contained within some streams of natural gas. Streams that contain commercial quantities of natural gas liquids are called wet gas, and those with little or no liquids present are known as dry gas (see earlier text).

Chemical manufacturers use ethane in making ethylene, an important petrochemical. Butane and propane, and mixtures of the two, are classified as LPG that is used chiefly as a heating fuel in industry and homes. Pentane, hexane, and heptane are collectively referred to as gas condensate (natural gasoline, casinghead gasoline, natural gas gasoline). However, at high pressures, such as those existing in the deeper fields, the density of the gas increases and the density of the oil decreases until they form a single phase in the reservoir.

Wet natural gas contains natural gasoline in vapor form. The wet gas, also known as casinghead gas, is chiefly a mixture of methane, ethane, and the volatile hydrocarbons propane, butane, pentane (C$_5$H$_{12}$), hexane (C$_6$H$_{14}$), and heptane (C$_7$H$_{16}$). The latter three hydrocarbons form the main constituents of natural gasoline, which is recovered in refineries in liquid form mainly by absorption or compression processes. Pentane, hexane, and heptane are liquids under normal atmospheric conditions and are the chief components of ordinary refinery gasoline. Natural gasoline is used as blending stock for refinery gasoline and may be cracked to produce lower-boiling products, such as ethylene, propylene, and butylene. Caution should be taken not to confuse natural gasoline with straight-run gasoline (often also incorrectly referred to as natural gasoline), which is the gasoline distilled unchanged from petroleum.

The various tests that are applied to specifications for this group of low-boiling liquids will be referenced in the chapters dealing with LPG (Chapter 4) and gasoline (Chapter 5).

1.3.4 Opportunity Crudes

There is also the need for a refinery to be configured to accommodate opportunity crude oils and/or high-acid crude oils, which, for many purposes, are often included with heavy feedstocks.

Opportunity crude oils are either new crude oils with unknown or poorly understood processing issues or are existing crude oils with well-known processing concerns. Opportunity crude oils are often, but not always, heavy crude oils but in either case are more difficult to desalt, most commonly due to high solid content, high levels of acidity, viscosity, electrical conductivity, or contaminants. They may also be oils that are incompatible, causing excessive equipment fouling when processed either in blends or separately.

Typically, 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, b). A controlled visbreaking treatment would clean up such crude oils by removing these undesirable constituents (which, if not removed, would cause problems further down the refinery sequence) as coke or sediment.

In addition to taking preventative measures 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 it can be valued appropriately, and management of the crude processing can be planned meticulously.

Compatibility of opportunity crudes with other opportunity crudes and with conventional crude oil and heavy oil is a very important property to consider when making decisions regarding which crude to purchase. Blending crudes that are incompatible can lead to extensive fouling and processing difficulties due to unstable asphaltene constituents (Speight, 2014a). These problems can quickly reduce the benefits of purchasing the opportunity crude in the first place. For example, extensive fouling in the crude preheat train may occur resulting in decreased energy efficiency, increased emissions of carbon dioxide, and increased frequency at which heat exchangers need to be cleaned. In a worst-case scenario, crude throughput may be reduced leading to significant financial losses.

Opportunity crude oils, while offering initial pricing advantages, may have composition problems that can cause severe problems at the refinery, harming infrastructure, yield, and profitability. Before refining, there is the need for comprehensive evaluations of opportunity crudes, giving the potential buyer and seller the needed data to make informed decisions regarding fair pricing and the suitability of a particular opportunity crude oil for a refinery. This will assist the refiner to manage the ever-changing crude oil quality input to a refinery—including quality and quantity requirements and situations, crude oil variations, contractual specifications, and risks associated with such opportunity crudes.

1.3.5 High-Acid Crudes

Acidity in crude oils is typically caused by the presence of naphthenic acids, which are natural constituents of petroleum, where they evolve through the oxidation of naphthenes (cycloalkanes). Initially, the presence of these acidic species
was suggested due to process artifacts formed during refining processes—and this may still be the case in some instances. However, it was shown that only a small quantity of acids was produced during these processes (Constantinides and Arich, 1967). Currently, it is generally assumed that acids may have been incorporated into the oil from three different sources: (i) acidic compounds found in source rocks, derived from the original organic matter that created the crude oil (plants and animals); (ii) neo-formed acids during biodegradation (although the high-acid concentration in biodegraded oils is believed to be related principally to the removal of nonacidic compounds, leading to a relative increase in the acid concentration levels); and (iii) acids that are derived from the bacteria themselves, for example, from cell walls that the organisms leave behind when their life cycle is completed (Mackenzie et al., 1981; Thorn and Aiken, 1998; Meredith et al., 2000; Tomczyk et al., 2001; Watson et al., 2002; Wilkes et al., 2003; Barth et al., 2004; Kim et al., 2005; Fafet et al., 2008).

The naphthenic acid subclass of the oxygen-containing species known as naphthenic acids and the term naphthenic acids is commonly used to describe an isomeric mixture of carboxylic acids (predominantly monocarboxylic acids) containing one or several saturated fused alicyclic rings (Hell and Medinger, 1874; Lochte, 1952; Ney et al., 1943; Tomczyk et al., 2001; Rodgers et al., 2002; Barrow et al., 2003; Clemente et al., 2003a, b; Zhao et al., 2012). However, in petroleum terminology, it has become customary to use this term to describe the whole range of organic acids found in crude oils; species such as phenols and other acidic species are often included in the naphthenic acid category (Speight, 2014b).

High-acid crude oils (Speight, 2014a, b) cause corrosion in the refinery—corrosion is predominant at temperatures in excess of 180°C (355°F) (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 that are shown to accelerate the hydrolysis reactions are inorganic clays and organic acids.

1.3.6 Foamy Oil

Foamy oil is oil-continuous foam that contains dispersed gas bubbles produced at the wellhead from heavy oil reservoirs under solution gas drive. The nature of the gas dispersions in oil distinguishes foamy oil behavior from conventional heavy oil. The gas that comes out of solution in the reservoir does not coalesce into large gas bubbles or into a continuous flowing gas phase. Instead, it remains as small bubbles entrained in the crude oil, keeping the effective oil viscosity low while providing expansive energy that helps drive the oil toward producing. Foamy oil accounts for unusually high production in heavy oil reservoirs under solution gas drive.

Thus, foamy oil is formed in solution gas drive reservoirs when gas is released from solution as reservoir pressure declines. It has been noted that the oil at the wellhead of these heavy-oil reservoirs resembles the form of foam, hence the term foamy oil. The gas initially exists in the form of small bubbles within individual pores in the rock. As time passes and pressure continues to decline, the bubbles grow to fill the pores. With further declines in pressure, the bubbles created in different locations become large enough to coalesce into a continuous gas phase. Once the gas phase becomes continuous (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 production gas–oil ratio increases rapidly after the critical.

Before analysis, the foam should be dismissed either by use of an appropriate separator vessel or by use of antifoaming agents. However, modification of the separator design may not always be feasible because of the limited space at many wellhead facilities, especially offshore platforms. Therefore, chemical additives (antifoaming agents, foam inhibitors) are employed to prevent or break up the foam. In the case of antifoaming agents, analysts must (i) determine the chemical nature of the agents, (ii) remove the agents prior to commencing analysis, and (iii) if item 2 is not possible or difficult, ensure that the presence of these agents does not interfere with the test method result.

1.3.7 Oil from Shale

One of the newest terms in the petroleum lexicon arbitrarily named (even erroneously named) shale oil is the crude oil that is produced from tight shale formation and should not be confused with shale oil, which is the oil produced by the thermal treatment of oil shale and the decomposition of kerogen contained therein (Speight, 2012b). The tight shale formations are those same formations that produce gas (tight gas) (Speight, 2013b). The introduction of the term shale oil to define crude oil from tight shale formations is the latest term to add confusion to the system of nomenclature of petroleum–heavy oil–bitumen materials. The term has been used without any consideration of the original term shale oil produced by the thermal decomposition of kerogen in oil shale. It is not quite analogous, but is certainly similarly confusing, to the term black oil that has been used to define petroleum by color rather than by any meaningful properties.
Typical of the oil from tight shale formations is the Bakken crude oil, which is a light crude oil. Briefly, Bakken crude oil is a light sweet (low-sulfur) crude oil that has a relatively high proportion of volatile constituents. The production of the oil yields not only petroleum but also a significant amount of volatile gases (including propane and butane) and low-boiling liquids (such as pentane and natural gasoline), which are often referred to collectively as (low-boiling or light) naphtha. By definition, natural gasoline (sometime also referred to as gas condensate) is a mixture of low-boiling liquid hydrocarbons isolated from petroleum and natural gas wells suitable for blending with light naphtha and/or refinery gasoline (Mokhatab et al., 2006; Speight, 2007, 2014a). Because of the presence of low-boiling hydrocarbons, light naphtha can become extremely explosive, even at relatively low ambient temperatures. Some of these gases may be burned off (flared) at the field wellhead, but others remain in the liquid products extracted from the well (Speight, 2014a).

The liquid stream produced from the Bakken formation will include the crude oil, the low-boiling liquids, and gases that were not flared, along with the materials and by-products of the fracking process. These products are then mechanically separated into three streams: (i) produced salt water, often referred to as brine; (ii) gases; and (iii) petroleum liquids, which include condensates, natural gas liquids, and light oil. Depending on the effectiveness and appropriate calibration of the separation equipment, which is controlled by the oil producers, varying quantities of gases remain dissolved and/or mixed in the liquids, and the whole is then transported from the separation equipment to the well-pad storage tanks, where emissions of volatile hydrocarbons have been detected as emanating from the oil.

Bakken crude oil is considered to be a low-sulfur (sweet) crude oil, and there have been increasing observations of elevated levels of hydrogen sulfide (H$_2$S) in the oil. Hydrogen sulfide is a toxic, highly flammable, corrosive, explosive gas (hydrogen sulfide), and there have been increasing observations of elevated levels of hydrogen sulfide in Bakken oil.

1.3.8 Heavy Oil

Heavy oil (heavy crude oil) is more viscous than conventional crude oil and has a lower mobility in the reservoir but can be recovered through a well from the reservoir by the application of secondary or enhanced recovery methods (Speight, 2009, 2013a, 2014a). The term heavy oil has also been arbitrarily used to describe both the heavy oils that require thermal stimulation of recovery from the reservoir and (incorrectly) to the bitumen in bituminous sand (tar sand, q.v.) formations from which the heavy bituminous material is recovered by a recovery operation other than the recognized enhanced oil recovery methods (Speight, 2009, 2014a).

When petroleum 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 petroleum. Heavy oil is a type of petroleum that is different from the conventional petroleum insofar as they are much more difficult to recover from the subsurface reservoir. These materials have a much higher viscosity (and lower API gravity) than conventional petroleum, and primary recovery of these petroleum types usually requires thermal stimulation of the reservoir (Speight, 2009, 2013a, b). Heavy oils are more difficult to recover from the subsurface reservoir than light oils. The definition of heavy oils is usually based on 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.

For many years, petroleum 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 vary depending upon the temperature at which distillation was terminated but usually vacuum residua are in the range 2–8° API (Speight, 2000 and references cited therein; Gary et al., 2007; Hsu and Robinson, 2006; Speight, 2014a; Speight and Ozum, 2002).

Heavy oil may also be called viscous oil—but the latter term has also been generally applied to petroleum products such a lubricating oil. More typically, and for the purposes of this book, viscous oils are those petroleum fractions and derived products that have higher-boiling points than distillate fuels and are liquid at, or slightly above, room temperature. The molecular constituents of these product oils contain 20 to ≥50 carbon atoms and distill at temperatures above 260°C (500°F). Examples include refinery streams such as gas oils, residua, cracked residua, and viscous oils as well as finished products such as white oil, lubricating oil, and other process oils.

The analysis of heavy oils is more complex than the analysis of hydrocarbon gases and lower-molecular-weight volatile liquids. In addition, the analysis of heavy oil may be complicated by issues related to handling—the higher viscosity of these oils makes them more difficult to sample, and the dark color can cause problems with some test methods.

Moreover, the types of molecular species present increases rapidly as the number of carbon atoms per molecule increases, and in addition, hydrocarbons in heavy oils are much more complex. Characterization does not (and should not) focus on identifying specific molecular structures but on classes of molecules (such as paraffins, naphthenes, aromatics, polycyclic compounds, and polar compounds). In addition to carbon
and hydrogen, heavy oils contain oxygen, sulfur, and nitrogen compounds, as well as trace quantities of metals (such as nickel and vanadium) may also be present. Determining the chemical form present for these elements provides additional important information.

Test methods of interest for the analysis of heavy oil (extra heavy oil and tar sand bitumen can be included here) include tests that measure physical properties such as density, refractive index, molecular weight, and boiling range; those methods that are used to measure chemical composition such as elemental and molecular structure analysis; and derivative methods that correlate measured properties with aspects of chemical composition (Speight, 2001, 2014a).

Test methods for conventional crude oil are generally applicable to heavy oil. However, depending upon the properties of the heavy oil, modification may be necessary as illustrated for tar sand bitumen (Section 1.3.10) (see also Wallace, 1988; Wallace et al., 1988).

1.3.9 Extra Heavy Oil

Briefly, *extra heavy oil* is a material that occurs in the solid or near-solid state and generally has mobility under reservoir conditions (Speight, 2009, 2013a, 2014a). *Extra heavy oil* is a recently evolved term that is of questionable scientific meaning and is subject to much verbal and written variation. While this material may resemble tar sand bitumen and does not flow easily, extra heavy oil can generally be recognized (for the purposes of this text) as being more viscous than heavy oil but having mobility in the reservoir—tar sand bitumen is typically incapable of mobility (free flow) under the conditions in the tar sand deposit.

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 belt 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 (that is higher than the pour point of the extra heavy oil) or due to other factors is variable and subject to localized conditions in the reservoir.

Test methods for conventional crude oil are not always applicable to extra heavy oil, and modification of the test method(s) may be necessary—as illustrated for tar sand bitumen (Section 1.3.10) (Wallace, 1988; Wallace et al., 1988).

1.3.10 Tar Sand Bitumen

*Tar sand* is the several rock types that contain an extremely viscous hydrocarbon that is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques (Speight, 2009, 2013a, 2014a).

More descriptively, *tar sand* is unconsolidated-to-consolidated sandstone or a porous carbonate rock, impregnated with bitumen. In simple terms, an unconsolidated rock approximates the consistency of dry or moist sand, and a consolidated rock may approximate the consistency of set concrete. Alternative names, such as *bituminous sand* or (in Canada) *oil sand*, are gradually finding usage, with the former name (*bituminous sand*) more technically correct. The term *oil sand* is also used in the same way as the term *tar sand*, and the terms are used interchangeably. The term *oil sand* is analogous to the term *oil shale*. Neither material contains oil, but oil is produced therefrom by application of thermal decomposition methods. It is important to understand that tar sand and the bitumen contained therein are different components of the deposit. The recovery of the bitumen, a hydrocarbonaceous material that can be converted into *synthetic crude oil* (Speight, 2014a), depends to a large degree on the composition and construction of the sands.

The molecular constituents found in tar sand bitumen also contain nitrogen, oxygen, sulfur, and metals (particularly nickel and vanadium) chemically bound in their molecular structures. Thus, it is chemically correct to refer to bitumen as a *hydrocarbonaceous* material, that is, a material that is composed predominantly of carbon and hydrogen but recognizing the presence of other atoms.

The term *bitumen* (also, on occasion, referred to as *native asphalt*, and *extra heavy oil*) includes a wide variety of reddish brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight. *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*.

On the basis of the definition of tar sand (earlier text), *bitumen*, also on occasion referred to as *native asphalt* and *extra heavy oil*, is a naturally occurring hydrocarbonaceous material that has little or no mobility under reservoir conditions and which cannot be recovered through a well by conventional oil well production methods including currently used enhanced recovery techniques; current methods involve mining for bitumen recovery (Speight, 2014a).

Because of the immobility of the bitumen, the permeability of the deposit is low, and passage of fluids through the deposit is prevented. 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 and has a much lower proportion of volatile constituents than a conventional crude oil (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

*Synthetic crude oil* is the hydrocarbon liquid that is produced from *bitumen*, by a variety of processes that involve
1.4 PETROLEUM REFINING

Petroleum is rarely used in its raw form and contains many thousands of different compounds that vary in molecular weight from methane (CH₄, molecular weight: 16) to more than 2000 (Speight, 2000, 2014a; Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007). This broad range in molecular weights results in boiling points that range from −160°C (−288°F) to temperatures in excess of 1100°C (2000°F) (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

Thus, a refinery is, of necessity, a complex network of integrated unit processes for the purpose of producing a variety of products from petroleum, usually by skeletal alteration, or even by alteration of the chemical type, of the petroleum constituents; and (iii) finishing—purification of various product streams by a variety of processes that essentially remove impurities from the product; for convenience, processes that accomplish molecular alteration, such as reforming, are also included in this category.

The separation and finishing processes may involve distillation or even treatment with a wash solution, either to remove impurities or, in the case of distillation, to produce a material boiling over a narrower range, and the chemistry of these processes is quite simple. Conversion processes are, in essence, processes that change the number of carbon atoms per molecule, alter the molecular hydrogen-to-carbon ratio, or change the molecular structure of the material without affecting the number of carbon atoms per molecule. These latter processes (isomerization processes) essentially change the shape of the molecule(s) and are used to improve the quality of the product (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

Thermal cracking processes are commonly used to convert petroleum residua into distillable liquid products, and examples of thermal cracking processes currently in use are visbreaking and coking (delayed coking, fluid coking, and flexicoking). In all of these processes, the simultaneous formation of sediment or coke limits the conversion to usable liquid products (Speight and Ozum 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

1.4.1 Visbreaking

The visbreaking process is used primarily as a means of reducing the viscosity of heavy feedstocks by controlled thermal decomposition insofar as the hot products are

### TABLE 1.3 Separation processes and conversion processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Action</th>
<th>Method</th>
<th>Purpose</th>
<th>Feedstock(s)</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric distillation</td>
<td>Separation</td>
<td>Thermal</td>
<td>Separate feedstock</td>
<td>Desalted crude oil</td>
<td>Gas, naphtha, gas oil, resid</td>
</tr>
<tr>
<td>Vacuum distillation</td>
<td>Separation</td>
<td>Thermal</td>
<td>Separate without cracking</td>
<td>Atmospheric resid</td>
<td>Gas oil, lube stock, residual</td>
</tr>
<tr>
<td>Conversion processes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalytic cracking</td>
<td>Alteration</td>
<td>Catalytic</td>
<td>Upgrading</td>
<td>Gas oil</td>
<td>Naphtha, petrochemical</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>feedstock</td>
</tr>
<tr>
<td></td>
<td>Polymerize</td>
<td>Thermal</td>
<td>Convert resid</td>
<td>Gas oil, coke distillate</td>
<td>Naphtha, petrochemical</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>feedstock</td>
</tr>
<tr>
<td></td>
<td>Hydrogenate</td>
<td>Catalytic</td>
<td>Convert to lower-boiling</td>
<td>Gas oil, resid</td>
<td>Lower-boiling products</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>products</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Decompose</td>
<td>Thermal</td>
<td>Reduce viscosity</td>
<td>Atmospheric resid</td>
<td>Distillate, fuel oil</td>
</tr>
</tbody>
</table>

petroleum feedstock from which a desired distribution of products is obtained. Nevertheless, refinery processes can be divided into three major types: (i) separation—division of petroleum into various streams (or fractions) depending on the nature of the crude material; (ii) conversion—production of salable materials from petroleum, usually by skeletal alteration, or even by alteration of the chemical type, of the petroleum constituents; and (iii) finishing—purification of various product streams by a variety of processes that essentially remove impurities from the product; for convenience, processes that accomplish molecular alteration, such as reforming, are also included in this category.
quenched before complete conversion can occur (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). However, the process is often plagued by sediment formation in the products. This sediment, or sludge, must be removed if the products are to meet fuel oil specifications.

The process uses the mild thermal cracking (partial conversion) as a relatively low-cost and low-severity approach to improving the viscosity characteristics of the residue without attempting significant conversion to distillates. Low residence times are required to avoid polymerization and coking reactions, although additives can help to suppress coke deposits on the tubes of the furnace.

A visbreaking unit consists of a reaction furnace, followed by quenching with a recycled oil, and fractionation of the product mixture (Speight, 2000, 2014a; Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007). All of the reaction in this process occurs as the oil flows through the tubes of the reaction furnace. The severity of the process is controlled by the flow rate through the furnace and the temperature; typical conditions are 475–500°C (885–930°F) at the furnace exit with a residence time of 1–3min, with operation for 3–6 months on stream (continuous use) is possible before the furnace tubes cleaned and the coke removed. The operating pressure in the furnace tubes can range from 0.7 to 5MPa depending on the degree of vaporization and the residence time desired. For a given furnace tube volume, a lower operating pressure will reduce the actual residence time of the liquid phase.

1.4.2 Coking

Coking, as the term is used in the petroleum industry, is a process for converting non-distillable fractions (residua) of petroleum to lower-boiling products and coke. Coking is often used in preference to catalytic cracking because of the presence of metals and nitrogen components that poison catalysts (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

There are several coking processes: delayed coking, fluid coking, and flexicoking as well as several other variations.

Delayed coking is the oldest, most widely used process and has changed very little in the five or more decades in which it has been on stream in refineries.

In the semi-continuous process, the residuum or other heavy feedstock is heated to the cracking/coking temperature (>350°C, >660°F); but usually at temperatures on the order of 480°C (895°F) and the hot liquid is charged, usually by upflow, to the coke drum where the coking reactions occur. Liquid and gaseous products pass to the fractionator for separation and coke deposits in the drum. The coke drums are arranged in pairs, one on stream and the other off stream, and used alternately to allow continuous processing. The process can be operated on a cycle, typically 24–48h.

The overhead oil is fractionated into fuel gas (ethane and lower-molecular-weight gases), propane–propylene, butane–butene, naphtha, light gas oil, and heavy gas oil. Yields and product quality vary widely due to the broad range of feedstock types charged to the delayed coking process. The function of the coke drum is to provide the residence time required for the coking reactions and to accumulate the coke. Hydraulic cutters are used to remove coke from the drum.

Fluid coking is a continuous fluidized solid process that cracks feed thermally over heated coke particles in a reactor vessel to gas, liquid products, and coke. Heat for the process is supplied by partial combustion of the coke, with the remaining coke being drawn as product. The new coke is deposited in a thin fresh layer on the outside surface of the circulating coke particle.

Small particles of coke made in the process circulate in a fluidized state between the vessels and are the heat transfer medium. Thus, the process requires no high-temperature preheat furnace. Fluid coking is carried out at essentially atmospheric pressure and temperatures in excess of 485°C (900°F) with residence times of the order of 15–30s. The longer residence time is in direct contrast to the delayed coking process, in which the coking reactions are allowed to proceed to completion. This is evident from the somewhat higher liquid yields observed in many fluid coking processes. However, the products from a fluid coker may contain more olefin species and be less desirable for downstream processing.

The flexicoking process is a modification of the fluid coking process that includes a gasifier adjoining the burner/regenerator to convert excess coke to a clean fuel gas with a heating value of about 90Btu/ft³. The coke gasification can be controlled to burn about 95% of the coke to maximize the production of coke gas or to operate at a reduced level to produce both gas and a coke. This flexibility permits adjustment for coke market conditions over a considerable range of feedstock properties.

The liquid products from the coker can, following cleanup via commercially available hydrodesulfurization technology (Speight, 2000, 2014a; Ancheyta and Speight, 2007), provide low-sulfur liquid fuels (<0.2% w/w sulfur). Coker naphtha has a boiling range up to 220°C (430°F), contains olefins, and must be upgraded by hydrogen processing for removal of olefins, sulfur, and nitrogen. They are then used conventionally for reforming to gasoline or chemical feedstock. Middle distillates, boiling in the range of 220–360°C (430–680°F), are also hydrogen treated for improved storage stability, sulfur removal, and nitrogen reduction. They can then be used as precursors to gasoline, diesel fuel, or fuel oil. The gas oil boiling up to 510°C (950°F) is usually low in metals and may be used as the feedstock for fluid catalytic cracking (Occelli, 2010).

Another major application for the coking processes is in upgrading heavy (high-viscosity) low-value petroleum into lighter products.
Petroleum coke is used principally as a fuel or, after calcining, for carbon electrodes. The feedstock from which the coke is produced controls the coke properties, especially sulfur, nitrogen, and metal content. A concentration effect tends to deposit the majority of the sulfur, nitrogen, and metals in the coke. Cokes exceeding about 2.5% sulfur content and 200ppm vanadium are mainly used, environmental regulations permitting for fuel or fuel additives. The properties of coke for non-fuel use include low sulfur, metals, and ash content as well as a definable physical structure.

### 1.4.3 Hydroprocessing

Hydroprocessing is the conversion of various feedstocks using the physical aspects of temperature, residence time, and the presence of hydrogen under pressure. Hydrotreating and hydrocracking are more conveniently subdivided into *hydrotreating* and *hydrocracking*.

*Hydrotreating* is defined as the lower-temperature removal of heteroatomic species by treatment of a feedstock or product in the presence of hydrogen. On the other hand, *hydrocracking* is the thermal decomposition (in the presence of hydrogen) of a feedstock in which carbon–carbon bonds are cleaved in addition to the removal of heteroatomic species (nitrogen oxygen, and sulfur) as the respective hydrogenated analogs (ammonia, NH₃; water, H₂O; and hydrogen sulfide, H₂S); in reality, hydrotreating and hydrocracking may occur simultaneously.

In contrast to the visbreaking process, in which the introductory principle is the production of products for use as fuel oil, the hydroprocessing is employed to produce a slate of products for use as liquid fuels.

### 1.5 PETROLEUM PRODUCTS

Petroleum products are any petroleum-based products that can be obtained by refining (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a) and comprise refinery gas, ethane, LPG, naphtha, gasoline, aviation fuel, marine fuel, kerosene, diesel oil, distillate fuel oil, residual fuel oil, gas oil, lubricants, white oil, grease, wax, asphalt, as well as coke. Petrochemical products are not included here.

Petroleum products are highly complex chemicals, and considerable effort is required to characterize their chemical and physical properties with a high degree of precision and accuracy. Indeed, the analysis of petroleum products is necessary to determine the properties that can assist in resolving a process problem as well as the properties that indicate the function and performance of the product in service.

Petroleum and the products obtained from refinery operations contain a variety of compounds, usually but not always hydrocarbons, and are not always immediately suitable for commercial use (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). As the number of carbon atoms in, for example, the paraffin series increases, the complexity of petroleum mixtures also rapidly increases. Consequently, detailed analysis of the individual constituents of the higher-boiling fractions becomes increasingly difficult, if not impossible.

Additionally, *classes (or types)* of hydrocarbons were, and still are, determined based on the capability to isolate them by separation techniques. The four fractional types into which petroleum is subdivided are paraffins, olefins, naphthenes, and aromatics. Paraffinic hydrocarbons include both normal and branched alkanes, whereas olefins refer to normal and branched alkenes that contain one or more double or triple carbon–carbon bonds. Naphthene (not to be confused with naphthalene) is a term specific to the petroleum industry that refers to the *saturated cyclic hydrocarbons* (cycloalkanes). Finally, the term *aromatics* includes all hydrocarbons containing one or more rings of the benzene-type structure.

These general definitions of the different fractions are subject to the many combinations of the hydrocarbon types (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a) and the action of the adsorbent or the solvent used in the separation procedure. For example, a compound containing 1 benzene-type ring (6 aromatic carbon atoms) that has 12 non-aromatic carbon atoms in alkyl side chains can be separated as an aromatic compound depending upon the adsorbent employed.

Although not directly derived from composition, the terms *light* or *heavy* or *sweet* and *sour* provide convenient terms for use in descriptions. For example, *light petroleum* (often referred to as conventional petroleum) is usually rich in low-boiling constituents and waxy molecules, while *heavy petroleum* contains greater proportions of higher-boiling, more aromatic, and heteroatom-containing (N-, O-, S-, and metal-containing) constituents. *Heavy oil* is more viscous than conventional petroleum and requires enhanced methods for recovery. *Bitumen* is near solid or solid and cannot be recovered by enhanced oil recovery methods (Speight, 2009, 2014a).

### 1.5.1 Types

The term *petroleum products* encompasses a wide range of chemical mixtures with a variable assortment of properties that vary from gases to liquids to solids. In order to understand the analytical method for petroleum products, a brief survey of the types of products and their general properties is warranted. More recently, the popularity of products from the Fischer–Tropsch process has increased ion prominence as has bio-oil—the product from the thermal decomposition of biomass (Speight, 2008, 2011b). Thus, for the sake of completeness, these definitions are also included.
1.5.1.1 Gases
Hydrocarbon products with four or less carbon atoms have boiling points that are lower than room temperature, and these products are gases at ambient temperature and pressure (Chapter 4). For example, natural gas (predominantly methane, CH4) is the lowest boiling and least complex of all hydrocarbons. Higher-boiling hydrocarbons up to n-octane (C8H18) may also be present in which case the gas is referred to as wet gas, which is usually processed (refined) to remove the high-boiling hydrocarbons (when isolated, the higher-boiling hydrocarbon mixture is often referred to as natural gas condensate). In fact, there are wells from which the predominant product is condensate.

Still gas is a term reserved for low-boiling hydrocarbon mixtures that represent the lowest-boiling fraction isolated from an atmospheric distillation unit (still) in the refinery. Typically, the still gas will contain methane, ethane (C2H6), propane (C3H8), and butane (C4H10), and their respective isomers. If cracked products have been recycled to the atmospheric distillation unit, the still gas may also contain volatile olefins such as ethylene (C2H4). The term fuel gas is often used interchangeably with still gas, but the term fuel gas is intended to denote the destination of the gaseous mixture, such as fuel for boilers, furnaces, or heaters, whereas the term still gas may be indicative of the use of the mixture for petrochemical production.

LPG is composed of propane (C3H8) and butane (C4H10)—the ratio of the two gases is variable and depends upon the ultimate use of the gas and the conditions of use—and is stored under pressure in order to keep the two hydrocarbons liquefied within the container. Before use, LPG passes through a pressure relief valve that causes a reduction in pressure, and the liquid vaporizes (gasifies). Winter-grade LPG is mostly propane, the lower boiling of the two gases that is easier to vaporize at lower temperatures. Summer-grade LPG contains higher amounts of butane.

Mixtures of these hydrocarbons are commonly encountered in material testing, and the composition varies depending upon the source and intended use of the material. Other non-hydrocarbon constituents of these mixtures are important analytes since they may be useful products or may be undesirable as a source of processing problems. Some of these constituents are helium-, hydrogen-, argon-, oxygen-, nitrogen-, carbon monoxide-, carbon dioxide-, sulfur-, and nitrogen-containing compounds, as well as higher-molecular-weight hydrocarbons. Desired testing of these hydrocarbon mixtures usually involves the determination of bulk physical or chemical properties and component speciation and quantitation.

1.5.1.2 Naphtha, Solvents, and Gasoline
Naphtha is the general term that is applied to refined, partly refined, or unrefined low-boiling liquid petroleum products (Chapter 5). Naphtha is prepared by any one of several methods including (i) fractionation of distillates or even crude petroleum, (ii) fluid catalytic cracking, (iii) solvent extraction, (iv) hydrogenation of distillates, (v) polymerization of unsaturated (olefin) compounds, and (vi) alkylation processes. Naphtha may also be a combination of product streams from more than one of these processes.

The term aliphatic naphtha refers to naphtha containing less than 0.1% benzene and with carbon numbers from C4 through C10. Aromatic naphtha has constituents composed of C6 through C16 hydrocarbons and contains significant quantities of aromatic hydrocarbons such as benzene (>0.1%), toluene, and xylene. The final gasoline product as a transport fuel is a carefully blended mixture having a predetermined octane value. Thus, gasoline is a complex mixture of hydrocarbons that boils below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have 4–12 carbon atoms.

The uses of petroleum naphtha include the following: (i) precursor to gasoline and other liquid fuels, (ii) solvents (diluents) for paints, (iii) dry-cleaning solvents, (iv) solvents for cutback asphalts, (v) solvents in rubber industry, and (vi) solvents for industrial extraction processes. Turpentine, the older and more conventional solvent for paints, has now been almost completely replaced by the cheaper and more abundant petroleum naphtha.

Petroleum solvents (also called naphtha) are valuable because of their good dissolving power. The wide range of naphtha available and the varying degree of volatility possible offer products suitable for many uses. Stoddard solvent is a petroleum distillate widely used as a dry-cleaning solvent and as a general cleaner and degreaser. It may also be used as paint thinner, as a solvent in some types of photocopier toners, in some types of printing inks, and in some adhesives. Stoddard solvent is considered to be a form of mineral spirits, white spirits, and naphtha; however, not all forms of mineral spirits, white spirits, and naphtha are considered to be Stoddard solvent. The solvent consists of linear and branched alkanes (30–50% v/v), cycloalkanes (30–40% v/v), and aromatic hydrocarbons (10–20% v/v).

Gasoline varies widely in composition, and even those with the same octane number may be quite different (Chapter 6). The variation in aromatic content as well as the variation in the content of normal paraffins, branched paraffins, cyclopentane derivatives, and cyclohexane derivatives all involves characteristics of any one individual crude oil and influence the octane number of the gasoline. However, in spite of the varied nomenclature of the refining industry, there is no one refining process that produces gasoline—gasoline is a blend of several refinery streams that is sold as gasoline after the inclusion of the necessary additives (Chapter 6) (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).
Automotive gasoline is a mixture of low-boiling hydrocarbon compounds suitable for use in spark-ignited internal combustion engines and having an octane rating of at least 60. Automotive gasoline contains 150 or more different chemical compounds, and the relative concentrations of the compounds vary considerably depending on the source of crude oil, refinery process, and product specifications. Typical hydrocarbon constituents are alkanes (4–8% v/v), alkenes (2–5% v/v), iso-alkanes (25–40% v/v), cycloalkanes (3–7% v/v), cycloalkenes (1–4% v/v), and aromatics (20–50% v/v). However, these proportions vary greatly.

Additives that have been used in gasoline include improvers for octave number, and other categories of compounds that may be added to gasoline include anti-knock agents, antioxidants, metal deactivators, lead scavengers, antitrust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes.

Aviation fuel occurs as two variations: (i) aviation gasoline and (ii) jet fuel (Chapter 7). Aviation gasoline, now usually found in use in light aircraft and older civil aircraft, has narrower boiling ranges than conventional (automobile) gasoline, that is, 38–170°C (100–340°F), compared to −1 to 200°C (30–390°F) for automobile gasoline. The narrower boiling range ensures better distribution of the vaporized fuel through the more complicated induction systems of aircraft engines. Since aircraft operate at altitudes where the prevailing pressure is relatively low—the pressure at 17,500 ft is 7.5 psi (0.5 atmosphere) compared to 14.8 psi (1.0 atmosphere) at the surface of the earth—the vapor pressure of aviation gasoline must be limited to reduce boiling in the tanks, fuel lines, and carburetors.

Aviation gasoline consists primarily of straight and branched alkanes and cycloalkanes. Aromatic hydrocarbons are limited to 20–25% v/v of the total mixture because of the smoke produced when they are burned. Jet fuel is classified as aviation turbine fuel, and, in the specifications, ratings relative to octave number are replaced with properties concerned with the ability of the fuel to burn cleanly.

Jet fuel is composed of distillate fractions and comprises both gasoline-type and kerosene-type jet fuels that meet specifications for use in aviation turbine units. Gasoline-type jet fuel includes naphtha constituents that distill between 100 and 250°C (212 and 480°F). This fuel is obtained by blending kerosene and gasoline or naphtha in such a way that the aromatic content does not exceed 25% v/v, with limits on the range of vapor pressure. Kerosene-type jet fuel is a middle distillate fraction used for aviation turbine power units. It has the same distillation characteristics and flash point as kerosene—between 150 and 300°C (300 and 570°F) but not generally above 250°C (480°F).

Volatility is an important property of all types of gasoline since it is related to performance and requires sufficient low-boiling hydrocarbons to vaporize easily in cold weather. The gasoline must also contain sufficient high-boiling hydrocarbons to remain a liquid in an engine’s fuel supply system during hotter periods.

1.5.1.3 Kerosene and Diesel Fuel

In the early days of the refining industry, before the onset of the automotive age, kerosene (kerosine) (Chapter 8) was the major refinery product but now is considered one of several other petroleum products after gasoline (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2011a, 2014a). Kerosene originated as a straight-run (distilled without molecular change) petroleum fraction that boiled between approximately 150 and 350°C (300 and 660°F). In the early days of petroleum refining, some crude oils contained kerosene fractions of very high quality, but other crude oils, such as those having a high proportion of asphaltic materials, had to be carefully refined to remove aromatics and sulfur compounds before a satisfactory kerosene fraction can be obtained.

Diesel fuel (Chapter 9) also forms part of the kerosene boiling range (or middle distillate group of products). Diesel fuels come in two broad groups: for high-speed engines in cars and trucks requiring a high-quality product, and lower-quality heavier diesel fuel for slower engines, such as in marine engines or for stationary power plants. However, like gasoline, in spite of the varied nomenclature of the refining industry, there is no one refinery process that produces diesel fuel and the diesel fuel for sale is actually a blend of several refinery streams that is then sold as diesel fuel after the inclusion of the necessary additives (Chapter 9) (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

The quality of diesel fuel is measured using the cetane number, which is a measure of the tendency of a diesel fuel to knock in a diesel engine, and the scale, from which the cetane number is derived, is based upon the ignition characteristics of two hydrocarbons: (i) n-hexadecane (cetane) and (ii) 2,3,4,5,6,7,8-heptamethylnonane.

1.5.1.4 Fuel oil

Fuel oil is generally subdivided into two main types: (i) distillate fuel oil (Chapter 10) and (ii) residual fuel oil (Chapter 11). However, the terms distillate fuel oil and residual fuel oil have lost some of their significance because fuel oils are now made for specific uses and may be distillates, residuals, or mixtures of the two. The terms domestic fuel oil, diesel fuel oil, and heavy fuel oil are more indicative of the uses of fuel oils. More often than not, fuel oil is prepared by using a visbreaker unit to perform mild thermal cracking on a residuum or a high-boiling distillate so that the product meets specifications (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

Distillate fuel oil is produced by distillation, has a definite boiling range, and does not contain constituents boiling above the specified distillation limit and does not contain
asphaltic constituents. A fuel oil that contains any amount of the residue from crude distillation or thermal cracking is residual fuel oil. Domestic fuel oil is fuel oil that is used primarily in the home and includes kerosene, stove oil, and furnace fuel oil. Diesel fuel oil is also a distillate fuel oil, while furnace fuel oil is similar to diesel fuel, but the proportion of cracked gas oil in diesel fuel is usually less since the high aromatic content of the cracked gas oil reduces the cetane number of the diesel fuel.

Stove oil is a straight-run (distilled without molecular change) fraction from crude oil, whereas other fuel oils are usually blends of two or more fractions that include high-boiling naphtha, light gas oil, heavy gas oil, and residuum. Cracked fractions such as light gas oil, heavy gas oil from catalytic cracking, and fractionator bottoms from catalytic cracking may also be used as blends to meet the specifications of the different fuel oils.

Heavy fuel oil includes a variety of oils ranging from distillates to residual oils that must be heated to 260°C (500°F) or higher before they can be used. In general, heavy fuel oils consist of residual oils blended with distillates to suit specific needs. Included among heavy fuel oils are various industrial oils; when used to fuel ships, heavy fuel oil is called bunker oil.

Fuel oil that is used for heating is graded from No. 1 Fuel Oil to No. 6 Fuel Oil and cover light distillate oils, medium distillate, heavy distillate, a blend of distillate and residue, and residue oil.

No. 1 fuel oil is a relatively low-boiling distillate (straight-run kerosene) consisting primarily of hydrocarbons in the range C₉–C₁₆ and is similar in composition to diesel fuel; the primary difference is in the additives. This fuel oil is used in atomizing burners that spray the fuel oil into a combustion chamber where the tiny droplets burn while in suspension. It is also used in asphalt coatings, enamels, paints, thinners, and varnishes.

No. 2 fuel oil is a petroleum distillate that may be referred to as domestic fuel oil or industrial fuel oil. The domestic fuel oil is usually lighter and straight-run refined; it is used primarily for home heating and to produce diesel fuel. Industrial distillate is the cracked type or a blend of both. It is used in smelting furnaces, ceramic kilns, and packaged boilers. It contains hydrocarbons in the C₁₁–C₂₀ range, whereas diesel fuel predominantly contains a mixture of C₁₀–C₁₉ hydrocarbons but contains less than 5% v/v polynuclear aromatic hydrocarbons (PNAs).

No. 6 fuel oil (also called Bunker C) is the residual material left after the light oil, naphtha, No. 1 fuel oil, and No. 2 fuel oil have been distilled from crude oil. No. 6 fuel oil can be blended directly to heavy fuel oil or made into asphalt. It is limited to commercial and industrial uses where sufficient heat is available to fluidize the oil for pumping and combustion. On the other hand, residual fuel oil is generally more complex in composition and impurities than distillate fuel oils and Bunker C. Because of the mode of manufacture, PNAs and their alkyl derivatives and metals are persistent constituents of No. 6 fuel oil.

1.5.1.5 White Oil, Insulating Oil, Insecticides

There is also a category of petroleum products known as white oil (Chapter 12) that generally falls into two classes: (i) technical white oil that is employed for cosmetics, textile lubrication, insecticide vehicles, and paper impregnation, and (ii) pharmaceutical white oil that is employed medically (e.g., as a laxative) or for the lubrication of food-handling machinery.

Insulating oil (as part of the white oil family) falls into two general classes: (i) oil used in transformers, circuit breakers, and oil-filled cables; and (ii) oil employed for impregnating the paper covering of wrapped cables. The first is highly refined fractions of low viscosity and comparatively high boiling range and resembles heavy burning oils, such as mineral seal oil, or the very light lubricating fractions known as nonviscous neutral oils. The second is usually highly viscous products and is often naphthenic distillate that is not usually highly refined.

Insecticides are derived from petroleum oil that can usually be applied in water-emulsion form and which have marked killing power for certain species of insects. For many applications for which their own effectiveness is too slight, the oils serve as carriers for active poisons, as in the household and livestock sprays.

Medicinal oil is a petroleum product that is used for medicinal purposes and must be ultrapure. For example, liquid paraffin is a clear water-white medicinal oil that is used to be given to miners to lubricate the alimentary tract and prevent coal dust buildup in the tract. Finally and by way of clarification, white spirit is not necessarily the same as white oil and is a refined distillate boiling in the naphtha–kerosene range. White spirit has a flash point above 30°C (86°F) and a distillation range of 135–200°C (275–390°F). Industrial spirit comprises light oils distilling between 30 and 200°C (86 and 390°F). There are several grades of industrial spirit, depending on the distillation range.

1.5.1.6 Lubricating Oil

Lubricating oil (Chapter 13) is distinguished from other fractions of crude oil by a usually high (>400°C, >750°F) boiling point, as well as high viscosity. Lubricating oil may be divided into many categories according to the types of service it is intended to perform. However, there are two main groups: (i) oils used in intermittent service, such as motor and aviation oils; and (ii) oils designed for continuous service such as turbine oils. Crankcase oil or motor oil may be either petroleum based or synthetic (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a; Speight and Exall, 2014).
Petroleum-based oils are produced from heavy-end crude oil distillates, which may be treated in several ways, such as (i) vacuum distillation, (ii) solvent treatment, (ii) acid treatment, or (iv) hydrotreating, to produce lubricating oils with the oils with necessary properties. Hydrocarbon types ranging from $C_{4}$ to $C_{50}$ occur in the various types of lubricating oils. The hydrocarbon constituents are predominantly mixtures of straight- and branched-chain hydrocarbons (alkanes), cycloalkanes, and aromatic hydrocarbons. PNAs, alkyl PNAs, and metals are also components of motor oils and crankcase oils, with the used oils typically having higher concentrations than the new unused oils.

### 1.5.1.7 Grease

Grease (Chapter 14) is a lubricating oil to which a thickening agent has been added for the purpose of holding the oil to surfaces that must be lubricated. The most widely used thickening agents are soaps of various kinds, and grease manufacture is essentially the mixing of soaps with lubricating oils.

Soap is made by chemically combining a metal hydroxide with a fat or fatty acid:

$$R \text{CO}_n \text{H} + \text{NaOH} \rightarrow R \text{CO}^-_n \text{Na}^+ + \text{H}_2\text{O}$$

**Soap**

The most common metal hydroxides used for this purpose are calcium hydroxide, sodium/potassium hydroxide (lye), lithium hydroxide, and barium hydroxide. Commonly used fatty acids for grease-making soaps come from cottonseed oil, tallow, and lard. Among the fatty acids used are stearic acid (from tallow), oleic acid (from cottonseed oil), and animal fatty acids (from lard).

### 1.5.1.8 Wax

Wax (Chapter 15) is of two general types: (i) paraffin wax in petroleum distillates and (ii) microcrystalline wax in petroleum residua.

**Paraffin wax** is a solid crystalline mixture of straight-chain (normal) hydrocarbons ranging from 20 to 30 carbon atoms per molecule, and even higher.

Paraffin wax is a solid crystalline mixture of straight-chain (normal) hydrocarbons ranging from $C_{20}$ to $C_{30}$, and possibly higher, that is, $\text{CH}_{2n}(\text{CH}_{2})_{n}\text{CH}_{3}$, where $n \geq 18$. It is distinguished by its solid state at ordinary temperatures (25°C, 77°F) and low viscosity (35–45 SUS at 99°C, 210°F) when melted. However, in contrast to petroleum wax, petroleum jelly (petroleum jelly), although solid at ordinary temperatures, does in fact contain both solid and liquid hydrocarbons. It is essentially a low-melting, ductile, microcrystalline wax.

**Microcrystalline waxes** form approximately 1–2% w/w of crude oil and are valuable products having numerous applications. These waxes are usually obtained from heavy lube distillates by solvent dewaxing and from tank bottom sludge by acid clay treatment. However, these crude wax products usually contain appreciable quantity (10–20% w/w) of residual oil and, as such, are not suitable for many applications such as paper coating, electrical insulation, textile printing, and polishes.

### 1.5.1.9 Residua and Asphalt

Residua (resids, sing.: resid, residuum) are the residues obtained from petroleum after nondestructive distillation has removed all the volatile materials (Chapter 16). The temperature of the distillation is usually maintained below 350°C (660°F) since the rate of thermal decomposition of petroleum constituents is minimal below this temperature, but the rate of thermal decomposition of petroleum constituents is substantially above 350°C (660°F). A residuum that has held above this temperature so that thermal decomposition has occurred is known as a cracked resid.

Asphalt (sometimes referred to as bitumen in Europe and other parts of the world) is produced from the distillation residuum (Chapter 16). In addition to road asphalt, a variety of asphalt grades for roofing and waterproofing are also produced. Asphalt has complex chemical and physical compositions that usually vary with the source of the crude oil, and it is produced to certain standards of hardness or softness in controlled vacuum distillation processes. There are wide variations in refinery operations and in the types of crude oils so different asphalts will be produced—for example, soft asphalts can be converted into harder asphalts by oxidation (air blowing). Asphalt is also produced by propane deasphalting and can be made softer by blending the hard asphalt with the extract obtained in the solvent treatment of lubricating oils (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

**Road oil** is liquid asphalt intended for easy application to earth roads and provides a strong base or a hard surface and will maintain satisfactory in-service performance for light traffic loads. **Cutback asphalt** is a mixture of hard asphalt that has been diluted with lower-boiling oil (aromatic naphtha or aromatic kerosene) to permit application as a liquid without drastic heating. **Asphalt emulsions** are typically oil-in-water emulsions that break on application to an earthen or stone surface—the asphaltic oil adheres to the stone, and the water disappears. In addition to their usefulness in road and soil stabilization, asphalt emulsions are also used for paper impregnation and waterproofing.

### 1.5.1.10 Coke, Carbon Black, and Graphite

Petroleum coke (Chapter 17) is the residue left by the destructive distillation (thermal cracking or coking) of petroleum residua. It consists mainly of carbon (90–95% w/w) and has low mineral matter ash content (measure as mineral ash). It is used as a feedstock in coke ovens for the steel industry, for heating purposes, for electrode manufacture, and for production of chemicals. The two most important
types are green coke and calcined coke. This product category (petroleum coke) also includes catalyst coke deposited on the catalyst during refining processes—this type of coke is not recoverable because of adherence to the catalyst and is removed by burning to produce fuel gas that may serve as process fuel gas. The composition of coke varies with the source of the crude oil but, in general, is insoluble in organic solvents and has a honeycomb-type appearance.

With the influx of heavy crude oil into refineries, the use of coke as a refinery fuel must proceed with some caution—the coke from heavy oil typically has a higher content of sulfur and nitrogen than coke from lighter crude oil. Both of these elements will produce unacceptable pollutants—sulfur oxides (SOx) and nitrogen oxides (NOx) produced during combustion of the coke are serious environmental contaminants (Speight, 2005).

Carbon black (Chapter 17) is produced from coke as a form of para-crystalline carbon that has a high surface-area-to-volume ratio. It is dissimilar to soot in its much higher surface-area-to-volume ratio and significantly lower content of PNAs. However, carbon black is widely used as a model compound for diesel soot for diesel oxidation experiments, as a filler in tires, and as a color pigment in plastics, paints, and ink.

Graphite (Chapter 17) is produced by treating petroleum coke in an oxygen-free oven at extremely high temperature. Graphite is also a naturally occurring mineral that occurs in two forms: (i) alpha and (ii) beta, which have identical physical properties but different crystal structures. All graphite produced from petroleum sources is of the alpha type.

1.5.1.11 Fischer–Tropsch Liquids and Bio-Oil

While not truly petroleum products in the literal sense, there are two other fuel products that must be included here: (i) Fischer–Tropsch liquids and (ii) bio-oil.

Fischer–Tropsch liquids are products (which vary from naphtha-type liquids to wax) produced by the Fischer–Tropsch synthesis using mixture of hydrogen and carbon monoxide (synthesis gas, syngas) as the feedstock (Davis and Occelli, 2010). The synthesis gas is produced by the gasification conversion of carbonaceous feedstock such as petroleum residua, coal, and biomass, and production of hydrocarbon products can be represented simply as follows:

\[ \text{CH}_{\text{resid,nc}} + \text{O}_2 \rightarrow \text{CO} + \text{H}_2 \]

\[ n\text{CO} + n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} \]

However, before conversion of the carbon monoxide and hydrogen to hydrocarbon products, several reactions are employed to adjust the hydrogen/carbon monoxide ratio. Most important is the water gas shift reaction in which additional hydrogen is produced (at the expense of carbon monoxide) to satisfy the hydrogen/carbon monoxide ratio necessary for the production of hydrocarbons:

\[ \text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2 \]

The boiling range of Fischer–Tropsch typically spans the naphtha and kerogen boiling ranges and is suitable for analysis by application of the standard test methods. With the suitable choice of a catalyst, the preference for products boiling in the naphtha range (<200°C, <390°F) or for product boiling in the diesel range (~150 to 300°C, 300 to 570°F) can be realized.

Bio-oil (pyrolysis oil, bio-crude) is the liquid product produced by the thermal decomposition (destructive distillation) of biomass at temperatures on the order of 500°C (930°F). The product is a synthetic crude oil and is of interest as a possible complement (eventually a substitute) to petroleum. The product can vary from a light tarry material to a free-flowing liquid—both require further refining to produce specification-grade fuels. Hydrocarbon moieties are predominant in the product, but the presence of varying levels of oxygen (depending upon the character of the feedstock) requires testament (using, e.g., hydrotreating) during refining.

In summary, the Fischer–Tropsch process produces hydrocarbon products of different molecular weights from a gas mixture of hydrogen and carbon monoxide (synthesis gas, syngas). The process uses various catalysts to produce linear hydrocarbons and oxygenates, including unrefined naphtha, diesel, and waxes. Analysis of these products is achieved using the relevant analytical test method presented in the following chapters.

1.5.2 Properties

Measurements of bulk properties are generally easy to perform and, therefore, quick and economical. Several properties may correlate well with certain compositional characteristics and are widely used as a quick and inexpensive means to determine those. The most important properties of a whole crude oil are its boiling-point distribution, its density (or API gravity), and its viscosity. The boiling-point distribution, boiling profile, or distillation assay gives the yield of the various distillation cuts, and selected properties of the fractions are usually determined (Table 1.4). It is a prime property in its own right that indicates how much gasoline and other transportation fuels can be made from petroleum without conversion. Density and viscosity are measured for secondary reasons. The former helps to estimate the paraffinic character of the oil, and the latter permits the assessment of its undesirable residual material that causes resistance to flow. Boiling-point distribution, density, and viscosity are easily measured and give a quick first evaluation of petroleum oil. Sulfur content, another crucial and primary property of a crude oil, is also readily determined.
Certain composite characterization values, calculated from density and mid-boiling point, correlate better with molecular composition than density alone (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a).

The acceptance of heavy oil and bitumen as refinery feedstocks has meant that the analytical techniques used for the lighter feedstocks have had to evolve to produce meaningful data that can be employed to assist in defining refinery scenarios for processing the feedstocks. In addition, selection of the most appropriate analytical procedures will aid in the predictability of feedstock behavior during refining. This same rationale can also be applied to feedstock behavior during recovery operations. Indeed, bitumen, a source of synthetic crude oil, is different from petroleum (Speight and Moschopedis, 1979; Speight, 2014a), and many of the test methods designed for petroleum may need modification before application to bitumen (Wallace, 1988; Wallace et al., 1988).

Thus, knowledge of the composition of petroleum and the resulting products allows the refiner to optimize the conversion of raw petroleum into high-value products. Modern refining uses a sophisticated combination of heat, catalyst, and hydrogen to rearrange the petroleum molecules into these products. Conversion processes include (i) coking, (ii) hydrocracking, and (iii) catalytic cracking to break large molecules into smaller fractions, as well as (iv) hydrotreating to reduce heteroatoms and aromatics creating environmentally acceptable products, and (v) isomerization and reforming to rearrange molecules to those with high value, for example, gasoline with a high octane number.

Also, knowledge of the molecular composition of petroleum allows environmental scientists to consider the biological impact of environmental exposure (Speight, 2005; Speight and Arjoon, 2012). Increasingly, petroleum is being produced and transported from remote areas of the world to refineries located closer to their markets. Although a miniscule fraction of that oil is released into the environment, the sheer volume involved has the potential for environmental exposure. Molecular composition is needed not only to identify the sources of contamination but also to understand the fate and effects of its potentially hazardous components.

In addition, knowledge of the composition of petroleum allows the geologist to answer questions of precursor–product relationships and conversion mechanisms. Biomarkers—molecules that retain the basic carbon skeletons of biological compounds from living organisms after losing functional groups through the maturation process—play an important role in such studies. The distribution of biomarker isomers can not only serve as fingerprints for oil/oil and oil/source correlation (to relate the source and reservoir) but also give

<table>
<thead>
<tr>
<th>Fraction*</th>
<th>Fraction</th>
<th>% Cumulative</th>
<th>Specific Gravity</th>
<th>API Gravity</th>
<th>Sulfur Wt %</th>
<th>Carbon Residue</th>
</tr>
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<tr>
<td></td>
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<tr>
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</tr>
<tr>
<td>2 50–75</td>
<td>122–167</td>
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<tr>
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<td>167–212</td>
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<td>0.0</td>
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<tr>
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<td>212–257</td>
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</tr>
<tr>
<td>5 125–150</td>
<td>257–302</td>
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<td>1.7</td>
<td>0.809 43.4</td>
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<tr>
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<td>302–347</td>
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<td>1.7</td>
<td>0.823 40.4</td>
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<tr>
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<td>2.8</td>
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<tr>
<td>8 200–225</td>
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<td>3.9</td>
<td>0.866 31.8</td>
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<tr>
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<td>437–482</td>
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<td>8.0</td>
<td>0.867 31.7</td>
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<tr>
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<td>30.8</td>
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<tr>
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<td>482–527</td>
<td>6.4</td>
<td>37.2</td>
<td>0.972 14.1</td>
<td>14.1</td>
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<tr>
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<td>527–572</td>
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<td>47.8</td>
<td>0.972 14.1</td>
<td>14.1</td>
<td>14.1</td>
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<tr>
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<td>&gt;572</td>
<td>49.5</td>
<td>97.3 39.6</td>
<td>39.6</td>
<td>39.6</td>
</tr>
</tbody>
</table>

*Distillation at 762 mmHg then at 40 mmHg for fractions 11–15.
geochemical information on organic source input (marine, lacustrine, or land-based sources), age, maturity, depositional environment (e.g., clay or carbonate, oxygen levels, salinity), and alteration (e.g., water washing, biodegradation) (Speight and Arjoon, 2012).

The need for the application of analytical techniques for petroleum and petroleum products has increased over the past three decades because of the change in feedstock composition. This has arisen because of the increased amounts of the heavier feedstocks that are now used to produce liquid products. Prior to the energy crises of the 1970s, the heavier feedstocks were used infrequently as sources of liquid fuels and were used to produce asphalt. Now these feedstocks have increased in value as sources of liquid fuels.

Because of the wide range of chemical and physical properties, a wide range of tests have been (and continue to be) developed to provide an indication of the means by which a particular feedstock should be processed. Initial inspection of the nature of the petroleum will provide deductions about the most logical means of refining or correlation of various properties to structural types present and hence attempted classification of the petroleum. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of their significance.

Having decided what characteristics are necessary, it then remains to describe the product in terms of a specification. This entails selecting suitable test methods and setting appropriate limits. Many specifications in widespread use have evolved usually by the addition of extra clauses (rarely is a clause deleted). This has resulted in unnecessary restrictions that, in turn, result in increased cost of the products specified.

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