3 Feedstock Composition

3.1 INTRODUCTION

Petroleum, heavy oil, and tar sand bitumen are not usually found where the precursors were laid down, but in reservoirs where accumulation occurs after it has migrated from the source rocks through geologic strata. In addition, the theory that the petroleum precursors form a mix that is often referred to as “protopetroleum” (also referred to as “primordial precursor soup” or “petroleum porridge”) is an acceptable generalization (Speight, 2014). And the molecular types in any specified fraction are limited by the nature of the precursors of petroleum, their chemical structures, and the physical conditions that are prevalent during the maturation (conversion of the precursors) processes.

This concept has resulted in the consideration of petroleum as a continuum of molecular types, and the nature of continuum is dictated by the proportions of the precursors that form the protopetroleum after which the prevalent conditions become operational in the formation of the final crude oil product. With this in mind, it might be anticipated that similar molecular types occur in heavy oil and bitumen as occurs in conventional petroleum. It then becomes a question of degree as well as molecular weight.

In the natural state, crude oil, heavy oil, extra heavy oil, and tar sand bitumen are not homogeneous materials, and the physical characteristics differ depending on where the material was produced. This is due to the fact that any of these feedstocks from different geographical locations will naturally have unique properties. In its natural, unrefined state, crude oil, heavy oil, extra heavy oil, and tar sand bitumen range in density and consistency from very thin, lightweight, and volatile fluidity to an extremely thick, semisolid (Speight, 2014). There is also a tremendous gradation in the color that ranges from a light, golden yellow (conventional crude oil) to black tar sand bitumen.

Thus, petroleum, heavy oil, and tar sand bitumen are not (within the individual categories) uniform materials, and the chemical and physical (fractional) composition of each of these refinery feedstocks can vary not only with the location and age of the reservoir or deposit but also with the depth of the individual well within the reservoir or deposit. On a molecular basis, the three feedstocks are complex mixtures containing (depending upon the feedstock) hydrocarbons with varying amounts of hydrocarbonaceous constituents that contain sulfur, oxygen, and nitrogen, as well as constituents containing vanadium, nickel, iron, and copper. The hydrocarbon content may be as high as 97% w/w, for example, in a light crude oil or less than 50% w/w in heavy crude oil and bitumen (Speight, 2014).

Heavy oil, bitumen, and residua (as a result of the concentration effect of distillation) contain more heteroatomic species and less hydrocarbon constituents than conventional crude oil. Thus, to obtain more gasoline and other liquid fuels, there have been different approaches to refining the heavier feedstocks as well as the recognition that knowledge of the constituents of these higher-boiling feedstocks is also of some importance. The problems encountered in processing the heavier feedstocks can be equated to the chemical character and the amount of complex, higher-boiling constituents in the feedstock. Refining these materials is not just a matter of applying know-how derived from refining conventional crude oils but requires knowledge of the chemical structure and chemical behavior of these more complex constituents.

The purpose of this chapter is to present a brief overview of the types of constituents that are found in petroleum, heavy oil, and bitumen and to also provide brief descriptions of the chemistry and physics of thermal decomposition.
3.2 ELEMENTAL COMPOSITION

The analysis of feedstocks for the percentages by weight of carbon, hydrogen, nitrogen, oxygen, and sulfur (elemental composition, ultimate composition) is perhaps the first method used to examine the general nature, and perform an evaluation, of a feedstock. The atomic ratios of the various elements to carbon (i.e., H/C, N/C, O/C, and S/C) are frequently used for indications of the overall character of the feedstock. It is also of value to determine the amounts of trace elements, such as vanadium and nickel, in a feedstock since these materials can have serious deleterious effects on catalyst performance during refining by catalytic processes.

For example, carbon content can be determined by the method designated for coal and coke (ASTM D3178, 2015) or by the method designated for municipal solid waste (ASTM E777, 2015). There are also methods designated for (1) hydrogen content, ASTM D1018 (2015), ASTM D3178 (2015), ASTM D3343 (2015), ASTM D3701 (2015), and ASTM E777 (2015); (2) nitrogen content, ASTM D3179 (2015), ASTM D3228 (2015), ASTM E258 (2015), and ASTM E778 (2015); (3) oxygen content, ASTM E385 (2015); and (4) sulfur content, ASTM D1266 (2015), ASTM D1552 (2015), ASTM D1757 (2015), ASTM D2622 (2015), ASTM D3177 (2015), ASTM D4045 (2015), and ASTM D4294 (2015). For all feedstocks, the higher the atomic hydrogen–carbon ratio, the higher is its value as refinery feedstock because of the lower hydrogen requirements for upgrading. Similarly, the lower the heteroatom content, the lower the hydrogen requirements for upgrading. Thus, inspection of the elemental composition of feedstocks is an initial indication of the quality of the feedstock and, with the molecular weight, indicates the molar hydrogen requirements for upgrading (Figure 3.1).

However, it has become apparent, with the introduction of the heavier feedstocks into refinery operations, that these ratios are not the only requirement for predicting feedstock character before refining. The use of more complex feedstocks (in terms of chemical composition) has added a new dimension to refining operations. Thus, although atomic ratios, as determined by elemental analyses, may be used on a comparative basis between feedstocks, there is now no guarantee that a particular feedstock will behave as predicted from these data. Product slates cannot be predicted accurately, if at all, from these ratios. Additional knowledge such as defining the various chemical reactions of the constituents as well as the reactions of these constituents with each other also plays a role in determining the processability of a feedstock.

![FIGURE 3.1 Atomic hydrogen/carbon ratio and molecular weight of feedstocks.](image-url)
Feedstock Composition

In summary, petroleum contains carbon, hydrogen, nitrogen, oxygen, sulfur, and metals (particularly nickel and vanadium), and the amounts of these elements in a whole series of crude oils vary over fairly narrow limits:

- Carbon: 83.0%–87.0%
- Hydrogen: 10.0%–14.0%
- Nitrogen: 0.1%–2.0%
- Oxygen: 0.05%–1.5%
- Sulfur: 0.05%–6.0%
- Metals: (Ni and V) <1000 ppm

This narrow range is contradictory to the wide variation in physical properties from the lighter, more mobile crude oils at one extreme to the heavier asphaltic crude oils at the other extreme (see also Charbonnier et al., 1969; Draper et al., 1977). And because of the narrow range of carbon and hydrogen content, it is not possible to classify petroleum on the basis of carbon content as coal is classified; carbon contents of coal can vary from as low as 75% w/w in lignite to 95% w/w in anthracite (Speight, 2013). Of course, other subdivisions are possible within the various carbon ranges of the coals, but petroleum is restricted to a much narrower range of elemental composition.

The elemental analysis of oil sand bitumen has also been widely reported (Speight, 1990, 2009), but the data suffer from the disadvantage that identification of the source is too general (i.e., Athabasca bitumen that covers several deposits) and is often not site specific. In addition, the analysis is quoted for separated bitumen, which may have been obtained by any one of several procedures and may therefore not be representative of the total bitumen on the sand. However, recent efforts have focused on a program to produce sound, reproducible data from samples for which the origin is carefully identified (Wallace et al., 1988).

Like conventional petroleum of the data that are available, the elemental composition of oil sand bitumen is generally constant and, like the data for petroleum, falls into a narrow range:

- Carbon: 83.4%–0.5%
- Hydrogen: 10.4%–0.2%
- Nitrogen: 0.4%–0.2%
- Oxygen: 1.0%–0.2%
- Sulfur: 0.05%–6.0%
- Metals: (Ni and V) >1000 ppm

The major exception to these narrow limits is the oxygen content that can vary from as little as 0.2% to as high as 4.5%. This is not surprising, since when oxygen is estimated by difference the analysis is subject to the accumulation of all of the errors in the other elemental data. In addition, bitumen is susceptible to aerial oxygen and the oxygen content is very dependent on sample history.

Although several generalities can be noted from the ultimate composition, these can only give indications of how the material might behave during processing.

The viscosity of tar sand bitumen is related to its hydrogen-to-carbon atomic ratio and hence the required supplementary heat energy for thermal extraction processes. It also affects the bitumen’s distillation curve or thermodynamic characteristics, its gravity, and its pour point. Atomic hydrogen-to-carbon ratios as low as 1.3 have been observed for tar sand bitumen, although an atomic hydrogen-to-carbon ratio of 1.5 is more typical. The higher the hydrogen–carbon ratio of bitumen, the higher is its value as refinery feedstock because of the lower hydrogen requirements. Elements related to the hydrogen–carbon ratio are distillation curve, bitumen gravity, pour point, and bitumen viscosity.
The occurrence of sulfur in bitumen as organic or elemental sulfur or in produced gas as compounds of oxygen and hydrogen is an expensive nuisance. It must be removed from the bitumen at some point in the upgrading and refining process. Sulfur contents of some tar sand bitumen can exceed 10% w/w. Elements related to sulfur content are hydrogen content, hydrogen–carbon ratio, nitrogen content, distillation curve, and viscosity.

The nitrogen content of tar sand bitumen can be as high as 1.3% by weight and nitrogen-containing constituents complicate the refining process by poisoning the catalysts employed in the refining process. Elements related to nitrogen content are sulfur content, hydrogen content, hydrogen–carbon ratio, bitumen viscosity, distillation profile, and viscosity.

Furthermore, heteroatoms in feedstocks affect every aspect of refining. The occurrence of sulfur in feedstocks as organic or elemental sulfur or in produced gas as compounds of oxygen \((\text{SO}_x)\) and hydrogen \((\text{H}_2\text{S})\) is an expensive aspect of refining. It must be removed at some point in the upgrading and refining process. Sulfur contents of many crude oil are on the order of 1% by weight, whereas the sulfur content of tar sand bitumen can exceed 5% or even 10% by weight. Of all of the hetero-elements, sulfur is usually the easiest to remove and many commercial catalysts are available that routinely remove 90% of the sulfur from a feedstock (Speight, 2000).

The nitrogen content of petroleum is usually less than 1% by weight, but the nitrogen content of tar sand bitumen can be as high as 1.5% by weight. The presence of nitrogen complicates refining by poisoning the catalysts employed in the various processes. Nitrogen is more difficult to remove than sulfur, and there are fewer catalysts that are specific for nitrogen. If the nitrogen is not removed, the potential for the production of nitrogen oxides \((\text{NO}_x)\) during processing and use becomes real.

Metals (particularly vanadium and nickel) are found in every most crude oils. Heavy oils and residua contain relatively high proportions of metals either in the form of salts or as organometallic constituents (such as the metalloporphyrins), which are extremely difficult to remove from the feedstock. Indeed, the nature of the process by which residua are produced virtually dictates that all the metals in the original crude oil are concentrated in the residuum (Speight, 2000). The metallic constituents that may actually volatilize under the distillation conditions and appear in the higher-boiling distillates are the exceptions here.

Metal constituents of feedstocks cause problems by poisoning the catalysts used for sulfur and nitrogen removal as well as the catalysts used in other processes such as catalytic cracking. Thus, serious attempts are being made to develop catalysts that can tolerate a high concentration of metals without serious loss of catalyst activity or catalyst life.

A variety of tests have been designated for the determination of metals in petroleum products (ASTM D1318, 2015; ASTM D3340, 2015; ASTM D3341, 2015; ASTM D3605, 2015). Determination of metals in whole feeds can be accomplished by combustion of the sample so that only inorganic ash remains. The ash can then be digested with an acid and the solution examined for metal species by atomic absorption spectroscopy or by inductively coupled argon plasma spectrometry.

### 3.3 CHEMICAL COMPOSITION

Crude oil, heavy oil, and tar sand bitumen contain an extreme range of organic functionality and molecular size. In fact, the variety is so great that it is unlikely that a complete compound-by-compound description for even a single crude oil would not be possible. As already noted, the composition of petroleum can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells are more than likely to produce petroleum with very different characteristics.

In very general terms (and as observed from elemental analyses), petroleum, heavy oil, bitumen, and residua are a complex composition of (1) hydrocarbons, (2) nitrogen compounds, (3) oxygen...
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compounds, (4) sulfur compounds, and (5) metallic constituents. However, this general definition is not adequate to describe the composition of petroleum as it relates to the behavior of these feedstocks. Indeed, the consideration of hydrogen-to-carbon atomic ratio, sulfur content, and API gravity is no longer adequate for the task of determining refining behavior.

Furthermore, the molecular composition of petroleum can be described in terms of three classes of compounds: saturates, aromatics, and compounds bearing heteroatoms (sulfur, oxygen, or nitrogen). Within each class, there are several families of related compounds: (1) saturated constituents include normal alkanes, branched alkanes, and cycloalkanes (paraffins, iso-paraffins, and naphthenes, in petroleum terms), (2) alkene constituents (olefins) are rare to the extent of being considered an oddity, (3) monoaromatic constituents range from benzene to multiple fused ring analogs (naphthalene, phenanthrene, etc.), (4) thiol constituents (mercaptan constituents) contain sulfur as do thioether derivatives and thiophenederivatives, and (5) nitrogen- and oxygen-containing constituents are more likely to be found in polar forms (pyridines, pyrroles, phenols, carboxylic acids, amides, etc.) than in nonpolar forms (such as ethers). The distribution and characteristics of these molecular species account for the rich variety of crude oils.

Feedstock behavior during refining is better addressed through the consideration of the molecular makeup of the feedstock (perhaps, by analogy, just as genetic makeup dictates human behavior). The occurrence of amphoteric species (i.e., compounds having a mixed acid/base nature) is rarely addressed, as well as the phenomenon of molecular size or the occurrence of specific functional types (Figure 3.4), which can play a major role in the interactions between the constituents of a feedstock. All of these items are important in determining the feedstock behavior during refining operations.

An understanding of the chemical types (or composition) of any feedstock can lead to an understanding of the chemical aspects of processing the feedstock. Processability is not only a matter of knowing the elemental composition of a feedstock; it is also a matter of understanding the bulk properties as they relate to the chemical or physical composition of the material. For example, it is difficult to understand, a priori, the process chemistry of various feedstocks from the elemental composition alone. From such data, it might be surmised that the major difference between a heavy crude oil and a more conventional material is the H/C atomic ratio alone. This property indicates that a heavy crude oil (having a lower H/C atomic ratio and being more aromatic in character) would require more hydrogen for upgrading to liquid fuels. This is indeed true, but much more information is necessary to understand the processability of the feedstock.

With the necessity of processing crude oil residua, heavy oil, and tar sand bitumen, to obtain more gasoline and other liquid fuels, there has been the recognition that knowledge of the constituents of these higher-boiling feedstocks is also of some importance. Indeed, the problems encountered in processing the heavier feedstocks can be equated to the chemical character and the amount of complex, higher-boiling constituents in the feedstock. Refining these materials is not just a matter of applying know-how derived from refining conventional crude oils but requires knowledge of the chemical structure and chemical behavior of these more complex constituents.

However, heavy crude oil and bitumen are extremely complex, and very little direct information can be obtained by distillation. It is not possible to isolate and identify the constituents of the heavier feedstocks (using analytical techniques that rely upon volatility). Other methods of identifying the chemical constituents must be employed. Such techniques include a myriad of fractionation procedures as well as methods designed to draw inferences related to the hydrocarbon skeletal structures and the nature of the heteroatomic functions.

The hydrocarbon content of petroleum may be as high as 97% by weight (e.g., in the lighter paraffinic crude oils) or as low as 50% by weight or less as illustrated by the heavy asphaltic crude oils. Nevertheless, crude oils with as little as 50% hydrocarbon components are still
assumed to retain most of the essential characteristics of the hydrocarbons. It is, nevertheless, the nonhydrocarbon (sulfur, oxygen, nitrogen, and metal) constituents that play a large part in determining the processability of the crude oil and will determine the processability of crude oil, heavy oil, and tar sand bitumen in the future (Speight, 2011). But there is more to the composition of petroleum than the hydrocarbon content. The inclusion of organic compounds of sulfur, nitrogen, and oxygen serves only to present crude oils as even more complex mixtures, and the appearance of appreciable amounts of these nonhydrocarbon compounds causes some concern in the refining of crude oils. Even though the concentration of nonhydrocarbon constituents (i.e., those organic compounds containing one or more sulfur, oxygen, or nitrogen atoms) in certain fractions may be quite small, they tend to concentrate in the higher-boiling fractions of petroleum. Indeed, their influence on the processability of the petroleum is important irrespective of their molecular size and the fraction in which they occur. It is, nevertheless, the nonhydrocarbon (sulfur, oxygen, nitrogen, and metal) constituents that play a large part in determining the processability of the crude oil and their influence on the processability of the petroleum is important irrespective of their molecular size (Green et al., 1989; Speight, 2000, 2014, 2015). The occurrence of organic compounds of sulfur, nitrogen, and oxygen serves only to present crude oil as even more complex mixture, and the appearance of appreciable amounts of these nonhydrocarbon compounds causes some concern in crude oil refining. The nonhydrocarbon constituents (i.e., those organic compounds containing one or more sulfur, oxygen, or nitrogen atoms) tend to concentrate in the higher-boiling fractions of petroleum (Speight, 2000). In addition, as the feedstock series progresses to higher-molecular-weight feedstocks from crude oil to heavy crude oil to tar sand bitumen, not only does the number of the constituents increase but the molecular complexity of the constituents also increases (Figure 3.2).

The presence of traces of nonhydrocarbon compounds can impart objectionable characteristics to finished products, leading to discoloration and/or lack of stability during storage. On the other
hand, catalyst poisoning and corrosion are the most noticeable effects during refining sequences when these compounds are present. It is therefore not surprising that considerable attention must be given to the nonhydrocarbon constituents of petroleum as the trend in the refining industry, of late, has been to process more heavy crude oil as well as residua that contain substantial proportions of these nonhydrocarbon materials.

### 3.3.1 Hydrocarbon Constituents

The isolation of pure compounds from petroleum is an exceedingly difficult task, and the overwhelming complexity of the hydrocarbon constituents of the higher-molecular-weight fractions and the presence of compounds of sulfur, oxygen, and nitrogen are the main causes for the difficulties encountered. It is difficult on the basis of the data obtained from synthesized hydrocarbons to determine the identity or even the similarity of the synthetic hydrocarbons to those that constitute many of the higher-boiling fractions of petroleum. Nevertheless, it has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups (Table 3.1). Olefin groups are not usually found in crude oils, and acetylene-type hydrocarbons are very rare indeed. It is therefore convenient to divide the hydrocarbon components of petroleum into the following three classes:

1. **Paraffins**, which are saturated hydrocarbons with straight or branched chains, but without any ring structure
2. **Naphthenes**, which are saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as “alicyclic hydrocarbons”)

#### TABLE 3.1

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated hydrocarbons</td>
<td></td>
</tr>
<tr>
<td>n-Paraffins</td>
<td></td>
</tr>
<tr>
<td>Iso-Paraffins and other branched paraffins</td>
<td></td>
</tr>
<tr>
<td>Cycloparaffins (naphthenes)</td>
<td></td>
</tr>
<tr>
<td>Condensed cycloparaffins (including steranes, hopanes)</td>
<td></td>
</tr>
<tr>
<td>Alkyl side chains on ring systems</td>
<td></td>
</tr>
</tbody>
</table>
| Unsaturated hydrocarbons     |  Olefins, nonindigenous; present in products of thermal reactions  
| Aromatic hydrocarbons        |  Benzene systems  
|                             |  Condensed aromatic systems  
|                             |  Condensed naphthene–aromatic systems  
|                             |  Alkyl side chains on ring systems  
| Saturated heteroatomic systems |  Alkyl sulfides  
|                             |  Cycloalkyl sulfides  
| Sulfides                     |  Alkyl side chains on ring systems  
| Aromatic heteroatomic systems |  Furans (single-ring and multi-ring systems)  
|                             |  Thiophenes (single-ring and multi-ring systems)  
|                             |  Pyrroles (single-ring and multi-ring systems)  
|                             |  Pyridines (single-ring and multi-ring systems)  
|                             |  Mixed heteroatomic systems  
|                             |  Amphoteric (acid–base systems)  
|                             |  Alkyl side chains on ring systems  

3. **Aromatics**, which are hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, which may be linked up with (substituted) naphthene rings and/or paraffinic side chains

### 3.3.1.1 Paraffin Hydrocarbons

The proportion of paraffins in crude oil varies with the type of crude, but within any one crude oil, the proportion of paraffinic hydrocarbons usually decreases with increasing molecular weight and there is a concomitant increase in aromaticity and the relative proportion of heteroatoms (nitrogen, oxygen, and sulfur) (Figure 3.2).

The relationship between the various hydrocarbon constituents of crude oils is one of hydrogen addition or hydrogen loss (Figure 3.3). This is an extremely important aspect of petroleum composition, and there is no reason to deny the occurrence of these interconversion schemes during the formation, maturation, and *in situ* alteration of petroleum. Indeed, a scheme of this type lends even more credence to the complexity of petroleum within the hydrocarbon series alone and also supports current contentions that the high-molecular-weight constituents (resin constituents and asphaltene constituents) are structurally related to the lower-boiling constituents rather than proposals that invoke the existence of highly condensed polynuclear aromatic systems.

The abundance of the different members of the same homologous series varies considerably in absolute and relative values. However, in any particular crude oil or crude oil fraction, there may be a small number of constituents forming the greater part of the fraction, and these have been referred to as the “predominant constituents” (Bestougeff, 1961). This generality may also apply to other constituents and is very dependent upon the nature of the source material as well as the relative amounts of the individual source materials prevailing during maturation conditions (Speight, 2014).

*Normal paraffin hydrocarbons* (n-paraffins, straight-chain paraffins) occur in varying proportions in most crude oils. In fact, paraffinic petroleum may contain up to 20%–50% by weight n-paraffins in the gas oil fraction. However, naphthenic or asphaltic crude oils sometimes contain only very small amounts of normal paraffins.

![FIGURE 3.3 Interrelationship of the hydrocarbon types in petroleum.](image-url)
Considerable quantities of iso-paraffins have been noted to be present in the straight-run gasoline fraction of petroleum. The 2- and 3-methyl derivatives are the most abundant, and the 4-methyl derivative is present in small amounts, if at all, and it is generally accepted that the slightly branched paraffins predominate over the highly branched materials. It seems that the iso-paraffins occur throughout the boiling range of petroleum fractions. The proportion tends to decrease with increasing boiling point; it appears that if the iso-paraffins are present in lubricating oils their amount is too small to have any significant influence on the physical properties of the lubricating oils.

As the molecular weight (or boiling point) of the petroleum fraction increases, there is a concomitant decrease in the amount of free paraffins in the fraction. In certain types of crude oil, there may be no paraffins at all in the vacuum gas oil (VGO) fraction. For example, in the paraffinic crude oils, free paraffins will separate as a part of the asphaltene fraction but in the naphthenic crude oils, free paraffins are not expected in the gas oil and asphaltene fractions. The vestiges of paraffins in the asphaltene fractions occur as alkyl side chains on aromatic and naphthenic systems. And, these alkyl chains can contain 20 or more carbon atoms (Speight, 1994, 2014).

### 3.3.1.2 Cycloparaffin Hydrocarbons

Although only a small number of representatives have been isolated so far, cyclohexane derivatives, cyclopentane derivatives, and decahydronaphthalene (decalin) derivatives (naphthenes) are largely represented in oil fractions. Petroleum also contains polycyclic naphthenes, such as terpenes, and such molecules (often designated bridge-ring hydrocarbons) occur even in the heavy gasoline fractions (boiling point 150°C–200°C, 300°F–390°F). Naphthene rings may be built up of a varying number of carbon atoms, and among the synthesized hydrocarbons there are individual constituents with rings of the three-, four-, five-, six-, seven-, and eight-carbon atoms. It is now generally believed that crude oil fractions contain chiefly five- and six-carbon rings. Only naphthenes with five- and six-membered rings have been isolated from the lower-boiling fractions. Thermodynamic studies show that naphthene rings with five- and six-carbon atoms are the most stable. The naphthenic acids contain chiefly cyclopentane as well as cyclohexane rings.

Cycloparaffin derivatives (naphthene derivatives) are represented in all fractions in which the constituent molecules contain more than five-carbon atoms. Several series of cycloparaffin derivatives, usually containing five- or six-membered rings or their combinations, occur as polycyclic structures. The content of cycloparaffin derivatives in petroleum varies up to 60% of the total hydrocarbons. However, the cycloparaffin content of different boiling range fractions of a crude oil may not vary considerably and generally remains within rather close limits. Nevertheless, the structure of these constituents may change within the same crude oil as a function of the molecular weight or boiling range of the individual fractions as well as from one crude oil to another.

The principal structural variation of naphthenes is the number of rings present in the molecule. The mono- and bicyclic naphthenes are generally the major types of cycloparaffin derivatives in the lower-boiling fractions of petroleum, with boiling point or molecular weight increased by the presence of alkyl chains. The higher-boiling fractions, such as the lubricating oils, may contain two to six rings per molecule. As the molecular weight (or boiling point) of the petroleum fraction increases, there is a concomitant increase in the amount of cycloparaffin (naphthene) species in the fraction. In the asphaltic (naphthenic) crude oils, the gas oil fraction can contain considerable amounts of naphthenic ring systems that increase even more in consideration of the molecular types in the asphaltenes. However, as the molecular weight of the fraction increases, the occurrence of condensed naphthene ring systems and alkyl-substituted naphthene ring systems increases.

There is also the premise that the naphthene ring systems carry alkyl chains that are generally shorter than the alkyl substituents carried by aromatic systems. There are indications from spectroscopic studies that the short chains (methyl and ethyl) appear to be characteristic substituents
of the aromatic portion of the molecule, whereas a limited number (one or two) of longer chains may be attached to the cycloparaffin rings. The total number of chains, which is in general four to six, as well as their length, increases according to the molecular weight of the naphthene–aromatic compounds.

In the asphaltene constituent, free condensed naphthenic ring systems may occur, but general observations favor the occurrence of combined aromatic–naphthenic systems that are variously substituted by alkyl systems. There is also general evidence that the aromatic systems are responsible for the polarity of the asphaltene constituents. The heteroatoms are favored to occur on or within the aromatic (pseudo-aromatic) systems (Speight, 1994, 2014).

3.3.1.3 Aromatic Hydrocarbons

The concept of the occurrence of identifiable aromatic systems in nature is a reality and the occurrence of monocyclic and polycyclic aromatic systems in natural product chemicals is well documented (Sakarnen and Ludwig, 1971; Durand, 1980; Weiss and Edwards, 1980). However, one source of aromatic systems that is often ignored is petroleum (Eglinton and Murphy, 1969; Tissot and Welte, 1978; Brooks and Welte, 1984). Therefore, attempts to identify such systems in the nonvolatile constituents of petroleum should be an integral part of the repertoire of the petroleum chemist as well as the domain of the natural product chemist.

Crude oil is a mixture of compounds and aromatic compounds are common to all petroleum, and it is the difference in extent that becomes evident upon examination of a series of petroleum. By far, the majority of these aromatics contain paraffinic chains, naphthenic rings, and aromatic rings side by side.

There is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight. However, aromatic hydrocarbons without the accompanying naphthenic rings or alkyl-substituted derivatives seem to be present in appreciable amounts only in the lower petroleum fractions. Thus, the limitation of instrumentation notwithstanding, it is not surprising that spectroscopic identification of such compounds has been concerned with these low-boiling aromatics.

All known aromatics are present in gasoline fractions, but the benzene content is usually low compared to the benzene homologues, such as toluene and the xylene isomer. In addition to the 1- and 2-methylnaphthalenes, other simple alkyl naphthalene derivatives have also been isolated from crude oil. Aromatics without naphthenic rings appear to be relatively rare in the heavier fractions of petroleum (e.g., lubricating oils). In the higher-molecular-weight fractions, the rings are usually condensed together. Thus, components with two aromatic rings are presumed to be naphthalene derivatives and those with three aromatic rings may be phenanthrene derivatives. Currently, and because of the consideration of the natural product origins of petroleum, phenanthrene derivatives are favored over anthracene derivatives.

In summation, all hydrocarbon compounds that have aromatic rings, in addition to the presence of alkyl chains and naphthenic rings within the same molecule, are classified as aromatic compounds. Many separation procedures that have been applied to petroleum (Speight, 2014, 2015) result in the isolation of a compound as an aromatic even if there is only one such ring (i.e., six-carbon atoms) that is substituted by many more than six-carbon nonaromatic atoms.

It should also be emphasized that in the higher-boiling petroleum fractions, many polycyclic structures occur in naphthene–aromatic systems. The naphthene–aromatic hydrocarbons, together with the naphthenic hydrocarbon series, form the major content of higher-boiling petroleum fractions. Usually, the different naphthene–aromatic components are classified according to the number of aromatic rings in their molecules. The first to be distinguished is the series with an equal number of aromatic and naphthenic rings. The first members of the bicyclic series C9–C11 are the simplest, such as the 1-methyl-, 2-methyl, and 4-methylindanes and 2-methyl- and 7-methyltetralin. Tetralin and methyl-, dimethyl-, methyl ethyl-, and tetramethyltetralin have been found in several crude oils, particularly in the heavier, naphthenic, crude oils and there are valid reasons to believe that this
increase in the number of rings and side-chain complexity continues into the heavy oil and bitumen feedstocks.

Of special interest in the present context are the aromatic systems that occur in the nonvolatile asphaltene fraction (Speight, 1994). These polycyclic aromatic systems are complex molecules that fall into a molecular weight and boiling range where very little is known about model compounds (Speight, 1994, 2014). There has not been much success in determining the nature of such systems in the higher-boiling constituents of petroleum, that is, the residua or nonvolatile constituents. In fact, it has been generally assumed that as the boiling point of a petroleum fraction increases, so does the number of condensed rings in a polycyclic aromatic system. To an extent, this is true but the simplicities of such assumptions cause an omission of other important structural constituents of the petroleum matrix, the alkyl substituents, the heteroatoms, and any polycyclic systems that are linked by alkyl chains or by heteroatoms.

The active principle is that petroleum is a continuum (Chapters 12 and 13) and has natural product origins (Long, 1979, 1981; Speight, 1981, 1994, 2014). As such, it might be anticipated that there is a continuum of aromatic 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 of the aromatic nucleus that are identified in the volatile fractions, or in any natural product counterparts, also apply to the nonvolatile fractions.

The application of thermal techniques to study the nature of the volatile thermal fragments from petroleum asphaltenes has produced some interesting data relating to the nature of the aromatic systems and the alkyl side chains in crude oil, heavy oil, and bitumen (Speight, 1971; Ritchie et al., 1979a,b; Schucker and Keweshan, 1980; Gallegos, 1981). These thermal techniques have produced strong evidence for the presence of small (1–4 rings) aromatic systems (Speight and Pancirov, 1984; Speight, 1987). There was a preponderance of single-ring (cycloparaffin and alkylbenzene) species as well as the domination of saturated material over aromatic material.

Further studies using pyrolysis/gas chromatography/mass spectrometry (py/gc/ms) showed that different constituents of the asphaltene fraction produce the same type of polycyclic aromatic systems in the volatile matter but the distribution was not constant (Speight and Pancirov, 1984). It was also possible to compute the hydrocarbon distribution from which a noteworthy point here is preponderance of single-ring (cycloparaffin and alkylbenzene) species as well as the domination of saturated material over aromatic material. The emphasis on low-molecular-weight material in the volatile products is to be anticipated on the basis that more complex systems remain as nonvolatile material and, in fact, are converted to coke.

One other point worthy of note is that the py/gc/ms program does not accommodate nitrogen and oxygen species whether or not they be associated with aromatic systems. This matter is resolved, in part, not only by the concentration of nitrogen and oxygen in the nonvolatile material (coke) but also by the overall low proportions of these heteroatoms originally present in the asphaltenes (Speight and Pancirov, 1984). The major drawback to the use of the py/gc/ms technique to the study of the aromatic systems in asphaltenes is the amount of material that remains as a nonvolatile residue.

Of all of the methods applied to determining the types of aromatic systems in petroleum asphaltenes, one with considerable potential, but given the least attention, is ultraviolet spectroscopy (Lee et al., 1981; Bjorseth, 1983). Typically, the ultraviolet spectrum of an asphaltene shows two major regions with very little fine structure. Interpretation of such a spectrum can only be made in general terms. However, the technique can add valuable information about the degree of condensation of polycyclic aromatic ring systems through the auspices of high-performance liquid chromatography (HPLC) (Lee et al., 1981; Bjorseth, 1983; Monin and Pelet, 1983; Felix et al., 1985; Killops and Readman, 1985; Speight, 1986). Indeed, when this approach is taken, the technique not only confirms the complex nature of the asphaltene fraction but also allows further detailed identifications to be made of the individual functional constituents of asphaltenes. The constituents of the fraction produce a multicomponent chromatogram, but subfractions produce a less complex and
much narrower chromatograph that may even approximate a single peak, which may prove much more difficult to separate by a detector.

These data provide strong indications of the ring-size distribution of the polycyclic aromatic systems in petroleum asphaltenes. For example, from an examination of various functional subfractions (Figures 3.4 and 3.5), it was shown that amphoteric species and basic nitrogen species contain polycyclic aromatic systems having two to six rings per system. On the other hand, acid subfractions (phenolic/carboxylic functions) and neutral polar subfractions (amides/imino functions) contain few if any polycyclic aromatic systems having more than three rings per system. Moreover, the differences in the functionality of the subfractions result in substantial differences in thermal and catalytic reactivity that can lead to unanticipated phase separation and, subsequently, coke formation in a thermal reactor as well as structural orientation on, and blocking of, the active sites on a catalyst. This is especially the case when the behavior of the functional types that occur in the various high-boiling fractions of heavy oil and tar sand bitumen is considered (Figure 3.6) (Speight, 2014).

In all cases, the evidence favored the preponderance of the smaller (one-to-four) ring systems (Speight, 1986). But perhaps what is more important about these investigations is that the data show that the asphaltene fraction is a complex mixture of compound types that confirms fractionation studies and cannot be adequately represented by any particular formula that is construed to be
average. Therefore, the concept of a large polycyclic aromatic ring system as the central feature of the asphaltene fraction must be abandoned for lack of evidence.

In summary, the premise is that petroleum is a natural product and that the aromatic systems are based on identifiable structural systems that are derived from natural product precursors.

### 3.3.1.4 Unsaturated Hydrocarbons

The presence of olefins (RCH=CHR\(^1\)) in petroleum has been under dispute for many years because there are investigators who claim that olefins are actually present. In fact, these claims usually refer to distilled fractions, and it is very difficult to entirely avoid cracking during the distillation process. Nevertheless, evidence for the presence of considerable proportions of olefins in Pennsylvanian crude oils has been obtained; spectroscopic and chemical methods showed that the crude oils, as well as all distillate fractions, contained up to 3% w/w olefins. Hence, although the opinion that petroleum does not contain olefins requires some revision, it is perhaps reasonable to assume that the Pennsylvania crude oils may hold an exceptional position and that olefins are present in crude oil in only a few special cases. The presence of diene derivatives (RCH=CH=CHR\(^1\)) and acetylene derivatives (RC≡CR\(^1\)) is considered to be extremely unlikely.

In summary, a variety of hydrocarbon compounds occur throughout petroleum. Although the amount of any particular hydrocarbon varies from one crude oil to another, the family from which that hydrocarbon arises is well represented.

### 3.3.2 Nonhydrocarbon Constituents

The previous sections present some indication of the types and nomenclature of the organic hydrocarbons that occur in various crude oils. Thus, it is not surprising that petroleum, which contains only hydrocarbons, is, in fact, an extremely complex mixture. The phenomenal increase in the number of possible isomers for the higher hydrocarbons makes it very difficult, if not impossible in most cases, to isolate individual members of any one series having more than, say, 12-carbon atoms.
Inclusion of organic compounds of nitrogen, oxygen, and sulfur serves only to present crude oil as an even more complex mixture than was originally conceived. Nevertheless, considerable progress has been made in the isolation and/or identification of the lower-molecular-weight hydrocarbons, as well as accurate estimations of the overall proportions of the hydrocarbon types present in petroleum. Indeed, it has been established that as the boiling point of the petroleum fraction increases, not only the number of the constituents but the molecular complexity of the constituents also increases (Figure 3.2) (Speight, 2000, 2014).

Crude oils contain appreciable amounts of organic nonhydrocarbon constituents, mainly sulfur-, nitrogen-, and oxygen-containing compounds and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the nonvolatile residues.

Although their concentration in certain fractions may be quite small, their influence is important. For example, the decomposition of inorganic salts suspended in the crude can cause serious breakdowns in refinery operations; the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. The presence of organic acid components, such as mercaptan derivatives and acid derivatives, can also promote metallic corrosion. In catalytic operations, passivation and/or poisoning of the catalyst can be caused by the deposition of traces of metals (vanadium and nickel) or by chemisorption of nitrogen-containing compounds on the catalyst, thus necessitating the frequent regeneration of the catalyst or its expensive replacement.

The presence of traces of nonhydrocarbons may impart objectionable characteristics in finished products, such as discoloration, lack of stability on storage, or a reduction in the effectiveness of organic lead antiknock additives. It is thus obvious that a more extensive knowledge of these compounds and of their characteristics could result in improved refining methods and even in finished products of better quality. The nonhydrocarbon compounds, particularly the porphyrrins and related compounds, are also of fundamental interest in the elucidation of the origin and nature of crude oils.

3.3.2.1 Sulfur Compounds

Although the concentration of heteroatom constituents in certain fractions may be quite small, their influence is important. For example, the decomposition of inorganic salts suspended in the crude can cause serious breakdowns in refinery operations; the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. The presence of organic acid components, such as mercaptan derivatives and acid derivatives, can also promote metallic corrosion. In catalytic operations, passivation and/or poisoning of the catalyst can be caused by the deposition of traces of metals (vanadium and nickel) or by the chemisorption of nitrogen-containing compounds on the catalyst, thus necessitating the frequent regeneration of the catalyst or its expensive replacement.

Sulfur compounds are among the most important heteroatomic constituents of petroleum, and although there are many varieties of sulfur compounds (Table 3.2) (Speight, 2000, 2014), the prevailing conditions during the formation, maturation, and even in situ alteration may dictate that
only preferred types exist in any particular crude oil. Nevertheless, sulfur compounds of one type or another are present in all crude oils (Thompson et al., 1976). In general, the higher the density of the crude oil (or the lower the API gravity of the crude oil) the higher the sulfur content and the total sulfur in the crude oil can vary from approximately 0.04% w/w for light crude oil to approximately 5.0% for heavy crude oil and tar sand bitumen. However, the sulfur content of crude oils produced from broad geographic regions varies with time, depending on the composition of newly discovered fields, particularly those in different geological environments.

The presence of sulfur compounds in finished petroleum products often produces harmful effects. For example, in gasoline, sulfur compounds are believed to promote the corrosion of engine parts, especially under winter conditions, when water-containing sulfur dioxide from the combustion may accumulate in the crankcase. In addition, mercaptan derivatives in hydrocarbon solution cause the corrosion of copper and brass in the presence of air and also affect lead susceptibility and color stability. Free sulfur is also corrosive, as are sulfide derivatives, disulfide derivatives, and thiophene derivatives, which are detrimental to the octane number response to tetraethyllead. However, gasoline with a sulfur content between 0.2% and 0.5% has been used without obvious harmful effect. In diesel fuels, sulfur compounds increase wear and can contribute to the formation of engine deposits. Although high sulfur content can sometimes be tolerated in industrial fuel oils,
the situation for lubricating oils is that a high content of sulfur compounds in lubricating oils seems to lower resistance to oxidation and increases the deposition of solids.

Although it is generally true that the proportion of sulfur increases with the boiling point during distillation (Speight, 2000, 2014), the middle fractions may actually contain more sulfur than higher-boiling fractions as a result of decomposition of the higher-molecular-weight compounds during the distillation. High sulfur content is generally considered harmful in most petroleum products, and the removal of sulfur compounds or their conversion to less deleterious types is an important part of refinery practice. The distribution of the various types of sulfur compounds varies markedly among crude oils of diverse origin as well as between the various heavy feedstocks, but fortunately some of the sulfur compounds in petroleum undergo thermal reactions at relatively low temperatures. If elemental sulfur is present in the oil, a reaction, with the evolution of hydrogen sulfide, begins at approximately 150°C (300°F) and is very rapid at 220°C (430°F), but organically bound sulfur compounds do not yield hydrogen sulfide until higher temperatures are reached. Hydrogen sulfide is, however, a common constituent of many crude oils, and some crude oils with >1% w/w sulfur are often accompanied by a gas having substantial properties of hydrogen sulfide.

Various thiophene derivatives have also been isolated from a variety of crude oils; benzothiophene derivatives are usually present in the higher-boiling petroleum fractions. On the other hand, disulfides are not regarded as true constituents of crude oil but are generally formed by the oxidation of thiols during processing:

\[
2R–SH + [O] \rightarrow R–S–S–R + H_2O
\]

### 3.3.2.2 Nitrogen Compounds

Nitrogen in petroleum may be classified arbitrarily as basic and nonbasic. The basic nitrogen compounds (Table 3.3), which are composed mainly of pyridine homologues and occur throughout the boiling ranges, have a decided tendency to exist in the higher-boiling fractions and residua. The nonbasic nitrogen compounds, which are usually of the pyrrole, indole, and carbazole types, also occur in the higher-boiling fractions and residua.

In general, the nitrogen content of crude oil is low and generally falls within the range 0.1%–0.9% w/w, although early work indicates that some crude oil may contain up to 2% nitrogen. However, crude oils with no detectable nitrogen or even trace amounts are not uncommon, but in general the more asphalitic the oil, the higher its nitrogen content. Insofar as an approximate correlation exists between the sulfur content and the API gravity of crude oils (Speight, 2000, 2014), there also exists a correlation between the nitrogen content and the API gravity of crude oil. It also follows that there is an approximate correlation between the nitrogen content and the carbon residue: the higher the nitrogen content, the higher the carbon residue. The presence of nitrogen in petroleum is of much greater significance in refinery operations than might be expected from the small amounts present. Nitrogen compounds can be responsible for the poisoning of cracking catalysts, and they also contribute to gum formation in such products as domestic fuel oil. The trend in recent years toward cutting deeper into the crude to obtain stocks for catalytic cracking has accentuated the harmful effects of the nitrogen compounds, which are concentrated largely in the higher-boiling portions.

Basic nitrogen compounds with a relatively low molecular weight can be extracted with dilute mineral acids; equally strong bases of higher molecular weight remain unextracted because of unfavorable partitioning between the oil and aqueous phases. A method has been developed in which the nitrogen compounds are classified as basic or nonbasic, depending on whether they can be titrated with perchloric acid in a 50:50 solution of glacial acetic acid and benzene. The application of this method has shown that the ratio of basic to total nitrogen is approximately constant (0 to 30 ± 0.05) irrespective of the source of the crude. Indeed, the ratio of basic to total nitrogen was found to be approximately constant throughout the entire range of distillate and residual fractions.
Nitrogen compounds extractable with dilute mineral acids from petroleum distillates were found to consist of alkyl pyridine derivatives, alkyl quinoline derivatives, and alkyl iso-quinoline derivatives carrying alkyl substituents, as well as pyridine derivatives in which the substituent was a cyclopentyl or cyclohexyl group. The compounds that cannot be extracted with dilute mineral acids contain the greater part of the nitrogen in petroleum and are generally of the carbazole, indole, and pyrrole types.
3.3.2.3 Oxygen Compounds

Oxygen in organic compounds can occur in a variety of forms (ROH, ArOH, ROR, RCO₂H, ArCO₂H, RCO₂R, ArCO₂R, R₂C=O as well as the cyclic furan derivatives, where R and R’ are alkyl groups and Ar is an aromatic group) in nature, so it is not surprising that the more common oxygen-containing compounds occur in petroleum (Speight, 2014). The total oxygen content of crude oil is usually less than 2% w/w, although larger amounts have been reported, but when the oxygen content is phenomenally high it may be that the oil has suffered prolonged exposure to the atmosphere either during or after production. However, the oxygen content of petroleum increases with the boiling point of the fractions examined; in fact, the nonvolatile residua may have oxygen contents up to 8% w/w. Although these high-molecular-weight compounds contain most of the oxygen in petroleum, little is known concerning their structure, but those of lower molecular weight have been investigated with considerably more success and have been shown to contain carboxylic acids and phenols.

It has generally been concluded that the carboxylic acids in petroleum with fewer than eight-carbon atoms per molecule are almost entirely aliphatic in nature; monocyclic acids begin at C₆ and predominate above C₁₄. This indicates that the structures of the carboxylic acids correspond with those of the hydrocarbons with which they are associated in the crude oil. In the range in which paraffins are the prevailing type of hydrocarbon, the aliphatic acids may be expected to predominate. Similarly, in the ranges in which monocycloparaffin derivatives and dicycloparaffin derivatives prevail, one may expect to find principally monocyclic and dicyclic acid derivatives, respectively.

Although comparisons are frequently made between the sulfur and nitrogen contents and such physical properties as the API gravity, it is not the same with the oxygen contents of crude oils. It is possible to postulate, and show, that such relationships exist. However, the ease with which some of the crude oil constituents can react with oxygen (aerial or dissolved) to incorporate oxygen functions into their molecular structure often renders the exercise somewhat futile if meaningful deductions are to be made.

Carboxylic acid derivatives (RCO₂H) may be less detrimental than other heteroatom constituents because there is the high potential for decarboxylation to a hydrocarbon and carbon dioxide at the temperatures (>340°C, >645°F) used during distillation of flashing (Speight and Francisco, 1990):

\[ RCO₂H \rightarrow RH + CO₂ \]

In addition to the carboxylic acids and phenolic compounds (ArOH, where Ar is an aromatic moiety), the presence of ketones (>C=O), esters (>C(=O)–OR), ethers (R–O–R), and anhydrides >C(=O)–O–(O=)=C< has been claimed for a variety of crude oils. However, the precise identification of these compounds is difficult because most of them occur in the higher-molecular-weight nonvolatile residua. They are claimed to be products of the air blowing of the residua, and their existence in virgin crude oil, heavy oil, or bitumen may yet need to be substantiated.

3.3.2.4 Metallic Constituents

Metallic constituents are found in every crude oil, and the concentrations have to be reduced to convert the oil to transportation fuel. Metals affect many upgrading processes and cause particular problems because they poison catalysts used for sulfur and nitrogen removal as well as other processes such as catalytic cracking. The trace metals Ni and V are generally orders of magnitude higher than other metals in petroleum, except when contaminated with coproduced brine salts (Na, Mg, Ca, Cl) or corrosion products gathered in transportation (Fe).
The occurrence of metallic constituents in crude oil is of considerably greater interest to the petroleum industry than might be expected from the very small amounts present. Even minute amounts of iron, copper, and particularly nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yields of gasoline. In high-temperature power generators, such as oil-fired gas turbines, the presence of metallic constituents, particularly vanadium in the fuel, may lead to ash deposits on the turbine rotors, thus reducing clearances and disturbing their balance. More particularly, damage by corrosion may be very severe. The ash resulting from the combustion of fuels containing sodium and especially vanadium reacts with refractory furnace linings to lower their fusion points and so cause their deterioration.

Thus, the ash residue left after burning of a crude oil is due to the presence of these metallic constituents, part of which occur as inorganic water-soluble salts (mainly chlorides and sulfates of sodium, potassium, magnesium, and calcium) in the water phase of crude oil emulsions (Abdel-Aal et al., 2016). These are removed in the desalting operations, either by evaporation of the water and subsequent water washing or by breaking the emulsion, thereby causing the original mineral content of the crude to be substantially reduced. Other metals are present in the form of oil-soluble organometallic compounds as complexes, metallic soaps, or in the form of colloidal suspensions, and the total ash from desalted crude oils is of the order of 0.1–100 mg/L. Metals are generally found only in the nonvolatile portion of crude oil (Altgelt and Boduszynski, 1994; Reynolds, 1998).

Two groups of elements appear in significant concentrations in the original crude oil associated with well-defined types of compounds. Zinc, titanium, calcium, and magnesium appear in the form of organometallic soaps with surface-active properties adsorbed in the water/oil interfaces and act as emulsion stabilizers. However, vanadium, copper, nickel, and part of the iron found in crude oils seem to be in a different class and are present as oil-soluble compounds. These metals are capable of complexing with pyrrole pigment compounds derived from chlorophyll and hemoglobin and are almost certain to have been present in plant and animal source materials. It is easy to surmise that the metals in question are present in such form, ending in the ash content. Evidence for the presence of several other metals in oil-soluble form has been produced, and thus, zinc, titanium, calcium, and magnesium compounds have been identified in addition to vanadium, nickel, iron, and copper. Examination of the analyses of a number of crude oil for iron, nickel, vanadium, and copper indicates a relatively high vanadium content, which usually exceeds that of nickel, although the reverse can also occur.

Distillation concentrates the metallic constituents in the residues (Reynolds, 1998), although some can appear in the higher-boiling distillates, but the latter may be due in part to entrainment. Nevertheless, there is evidence that a portion of the metallic constituents may occur in the distillates by volatilization of the organometallic compounds present in the petroleum. In fact, as the percentage of overhead obtained by vacuum distillation of a reduced crude is increased, the amount of metallic constituents in the overhead oil is also increased. The majority of the vanadium, nickel, iron, and copper in residual stocks may be precipitated along with the asphaltenes by hydrocarbon solvents. Thus, removal of the asphaltenes with n-pentane reduces the vanadium content of the oil by up to 95% with substantial reductions in the amounts of iron and nickel.

### 3.3.2.5 Porphyrins

Porphyrins are a naturally occurring chemical species that exist in petroleum and usually occur in the nonbasic portion of the nitrogen-containing concentrate (Bonnett, 1978; Reynolds, 1998). They are not usually considered among the usual nitrogen-containing constituents of petroleum, nor are they considered a metallo-containing organic material that also occurs in some crude oils. As a result of these early investigations, there arose the concept of porphyrins as biomarkers that could establish a link between compounds found in the geosphere and their corresponding biological precursors.
Porphyrrins are derivatives of porphine that consists of four pyrrole molecules joined by methine (–CH=) bridges (Figure 3.7). The methine bridges establish conjugated linkages between the component pyrrole nuclei, forming a more extended resonance system. Although the resulting structure retains much of the inherent character of the pyrrole components, the larger conjugated system gives increased aromatic character to the porphine molecule. Furthermore, the imine functions (–NH–) in the porphine system allow metals such as nickel to be included into the molecule through chelation (Figure 3.8).

A large number of different porphyrin compounds exist in nature or have been synthesized. Most of these compounds have substituents other than hydrogen on many of the ring carbons. The nature of the substituents on porphyrin rings determines the classification of a specific porphyrin compound into one of various types according to one common system of nomenclature (Bonnet, 1978). Porphyrins also have well-known trivial names or acronyms that are often in more common usage than the formal system of nomenclature. When one or two double bonds of a porphyrin are hydrogenated, a chlorin or a phlorin is the result. Chlorin derivatives are components of

![FIGURE 3.7 Porphine—the basic structure of porphyrins.](image1)

![FIGURE 3.8 Nickel chelate of porphine.](image2)
chlorophyll and possess an iso-cyclic ring formed by two methylene groups bridging a pyrrole-type carbon to a methine carbon. Geological porphyrins that contain this structural feature are assumed to be derived from chlorophylls. Etioporphyrin derivatives are also commonly found in geological materials and have no substituents (other than hydrogen) on the methine carbons. Benzoporphyrin derivatives and tetrahydrobenzoporphyrin derivatives have also been identified in geological materials. These compounds have either a benzene ring or a hydrogenated benzene ring fused onto a pyrrole unit.

Almost all crude oil, heavy oil, and bitumen contain detectable amounts of vanadium and nickel porphyrin derivatives. More mature, lighter crude oils usually contain only small amounts of these compounds. Heavy oils may contain large amounts of vanadium and nickel porphyrin derivatives. Vanadium concentrations of over 1000 ppm are known for some crude oil, and a substantial amount of the vanadium in these crude oils is chelated with porphyrins. In high-sulfur crude oil of marine origin, vanadium porphyrin derivatives are more abundant than nickel porphyrin derivatives. Low-sulfur crude oils of lacustrine origin usually contain more nickel porphyrin derivatives than vanadium porphyrin derivatives.

Of all the metals in the periodic table, only vanadium and nickel have been proven definitely to exist as chelates in significant amounts in a large number of crude oils and tar sand bitumen. Geochemical reasons for the absence of substantial quantities of porphyrins chelated with metals other than nickel and vanadium in crude oils, heavy oils, and tar sand bitumen have been advanced (Hodgson et al., 1967; Baker, 1969; Baker and Palmer, 1978; Baker and Louda, 1986; Filby and Van Berkel, 1987; Quirke, 1987).

If the vanadium and nickel contents of crude oils are measured and compared with porphyrin concentrations, it is usually found that not all the metal content can be accounted for as porphyrin constituents (Reynolds, 1998). In some crude oils, as little as 10% w/w of total metals appears to be chelated with porphyrins. Only rarely can all measured nickel and vanadium in a crude oil be accounted for as porphyrin type. Currently, some investigators believe that part of the vanadium and nickel in crude oils is chelated with ligands that are not porphyrins. These metal chelates are referred to as nonporphyrin metal chelates or complexes (Reynolds et al., 1987).

Finally, during the fractionation of petroleum, the metallic constituents (metalloporphyrins and nonporphyrin metal chelates) are concentrated in the asphaltene fraction. The deasphaltened oil contains smaller concentrations of porphyrins than the parent materials and usually very small concentrations of nonporphyrin metals.

### 3.4 CHEMICAL COMPOSITION BY DISTILLATION

Although distillation is presented in more detail elsewhere (Chapter 7), it is appropriate to mention distillation here insofar as it is a method by which the constituents of petroleum can be separated and identified. Distillation is a means of separating chemical compounds (usually liquids) through differences in the respective vapor pressures. In the mixture, the components evaporate such that the vapor has a composition determined by the chemical properties of the mixture. Distillation of a given component is possible, if the vapor has a higher proportion of the given component than the mixture. This is caused by the given component having a higher vapor pressure and a lower boiling point than the other components.

By the nature of the process, it is theoretically impossible to completely separate and purify the individual components of petroleum when the possible number of isomers is considered for the individual carbon numbers that occur within the paraffin family (Table 3.4). When other types of compounds are included, such as the aromatic derivatives and heteroatom derivatives, even though the maturation process might limit the possible number of isomeric permutations (Tissot and Welte, 1978), the potential number of compounds in petroleum is still (in a sense) astronomical.

However, petroleum can be separated into a variety of fractions on the basis of the boiling points of the petroleum constituents. Such fractions are primarily identified by their respective boiling points.
ranges and, to a lesser extent, by chemical composition. However, it is often obvious that as the boiling ranges increase, the nature of the constituents remains closely similar and it is the number of the substituents that caused the increase in boiling point. It is through the recognition of such phenomena that molecular design of the higher-boiling constituents can be achieved (Figure 3.9). Invoking the existence of structurally different constituents in the nonvolatile fractions from those identifiable constituents in the lower-boiling fractions is unnecessary (considering the nature of the precursors and maturation paths) and irrational (Speight, 1994, 2014). For example, the predominant types of condensed aromatic systems in petroleum are derivatives of phenanthrene and there it is to be anticipated that the higher peri-condensed homologues (Figure 3.10) will be present in resin constituents and asphaltene constituents rather than the derivatives of kata-condensed polynuclear aromatic system (Figure 3.11).

**TABLE 3.4**

<table>
<thead>
<tr>
<th>Number of Carbon Atoms</th>
<th>Boiling Point $n$-Isomer ($°C$)</th>
<th>Boiling Point $n$-Isomer ($°F$)</th>
<th>Number of Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>36</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>174</td>
<td>345</td>
<td>75</td>
</tr>
<tr>
<td>15</td>
<td>271</td>
<td>519</td>
<td>4,347</td>
</tr>
<tr>
<td>20</td>
<td>344</td>
<td>651</td>
<td>366,319</td>
</tr>
<tr>
<td>25</td>
<td>402</td>
<td>755</td>
<td>36,797,588</td>
</tr>
<tr>
<td>30</td>
<td>450</td>
<td>841</td>
<td>4,111,846,763</td>
</tr>
<tr>
<td>40</td>
<td>525</td>
<td>977</td>
<td>62,491,178,805,831</td>
</tr>
</tbody>
</table>

**FIGURE 3.9** Separation of petroleum constituents by distillation.
Methane is the main hydrocarbon component of petroleum gases with lesser amounts of ethane, propane, butane, iso-butane, and some C₃⁺ hydrocarbons. Other gases, such as hydrogen, carbon dioxide, hydrogen sulfide, and carbonyl sulfide, are also present.

Saturated constituents with lesser amounts of mono- and diaromatics dominate the naphtha fraction. While naphtha covers the boiling range of gasoline, most of the raw petroleum naphtha
molecules have low octane number. However, most raw naphtha is processed further and combined with other process naphtha and additives to formulate commercial gasoline.

Within the saturated constituents in petroleum gases and naphtha, every possible paraffin from methane (\( \text{CH}_4 \)) to \( n \)-decan (normal decane, \( n-\text{C}_{10}\text{H}_{22} \)) is present. Depending upon the source, one of these low-boiling paraffins may be the most abundant compound in a crude oil reaching several percent. The iso-paraffins begin at \( C_4 \) with iso-butane as the only isomer of \( n \)-butane. The number of isomers grows rapidly with carbon number, and there may be increased difficulty in dealing with multiple isomers during analysis.

In addition to aliphatic molecules, the saturated constituents consist of cycloalkanes (naphthenes) with predominantly five- or six-carbon rings. Methyl derivatives of cyclopentane and cyclohexane, which are commonly found at higher levels than the parent unsubstituted structures, may be present (Tissot and Welte, 1978). Fused ring dicycloalkane derivatives such as cis-decahydronaphthalene (cis-decalin) and trans-decahydronaphthalene (trans-decalin) and hexahydro-indane are also common, but bicyclic naphthene derivatives separated by a single bond, such as cyclohexyl cyclohexane, are not.

The numerous aromatic constituents in petroleum naphtha begin with benzene, but its \( C_1-C_3 \) alkylated derivatives are also present (Tissot and Welte, 1978). Each of the alkyl benzene homologues through the 20 isomeric \( C_4 \) alkyl benzenes has been isolated from crude oil along with various \( C_5 \) derivatives. Benzene derivatives having fused cycloparaffin rings (naphthene aromatics) such as indane and tetralin have been isolated along with a number of their methyl derivatives. Naphthalene is included in this fraction, while the 1- and 2-methyl naphthalene derivatives and higher homologues of fused two ring aromatics appear in the mid-distillate fraction.

Sulfur-containing compounds are the only heteroatom compounds to be found in this fraction (Mair, 1964; Rall et al., 1972). Usually, the total amount of the sulfur in this fraction accounts for less than 1% of the total sulfur in the crude oil. In naphtha from high-sulfur (sour) petroleum, 50%–70% of the sulfur may be in the form of mercaptan derivatives (thiol derivatives). Over 40 individual thiols have been identified, including all the isomeric \( C_1 \) to \( C_6 \) compounds plus some \( C_7 \) and \( C_8 \) isomers plus thiophenol (Rall et al., 1972). In naphtha from low-sulfur (sweet) crude oil, the sulfur is distributed between sulfides (thioether derivatives) and thiophene derivatives. In these cases, the sulfides may be in the form of both linear (alkyl sulfides) and five- or six-ring cyclic (thiacyclane) structures. The sulfur structure distribution tends to follow the distribution hydrocarbons; that is, naphthenic oils with a high cycloalkane content tend to have a high thiacyclane content. Typical alkyl thiophene derivatives in naphtha have multiple short side chains or exist as naphthene–thiophene derivatives (Rall et al., 1972). Methyl and ethyl disulfides have been confirmed to be present in some crude oils in analyses that minimized their possible formation by oxidative coupling of thiols (Aksenova and Kayanov, 1980; Freidлина and Skorova, 1980).

3.4.2 Middle Distillates

Saturated species are the major component in the mid-distillate fraction of petroleum but aromatics, which now include simple compounds with up to three aromatic rings, and heterocyclic compounds are present and represent a larger portion of the total. Kerosene, jet fuel, and diesel fuel are all derived from raw middle distillate, which can also be obtained from cracked and hydroprocessed refinery streams.

Within the saturated constituents, the concentration of \( n \)-paraffins decreases regularly from \( C_{11} \) to \( C_{20} \). Two isoprenoid species (pristane = 2,6,10,14-tetramethylpentadecane and phytane = 2,6,10,14-tetramethylhexadecane) are generally present in crude oils in sufficient concentration to be seen as irregular peaks alongside the \( n-C_{17} \) and \( n-C_{18} \) peaks in a gas chromatogram. These isoprene derivatives, believed to arise as fragments of ancient precursors, have relevance as simple biomarkers, to the genesis of petroleum. The distribution of pristane and phytane relative to their neighboring \( n-C_{17} \) and \( n-C_{18} \) peaks has been used to aid the identification of crude oils and to detect
the onset of biodegradation. The ratio of pristane to phytane has also been used for the assessment of the oxidation and reduction environment in which ancient organisms were converted into petroleum (Hunt, 1979).

Mono- and dicycloparaffin derivatives with five or six carbons per ring constitute the bulk of the naphthenes in the middle distillate boiling range, decreasing in concentration as the carbon number increases (Tissot and Welte, 1978), and the alkylated naphthenes may have a single long side chain as well as one or more methyl or ethyl groups. Similarly, substituted three-ring naphthenes have been detected by gas chromatography and adamantane has been found in crude oil (Hunt, 1979; Lee et al., 1981).

The most abundant aromatics in the mid-distillate boiling fractions are di- and tri-methyl naphthalene derivatives. Other one and two ring aromatics are undoubtedly present in small quantities as either naphthene or alkyl homologues in the C11–C20 range. In addition to these homologues of alkylbenzenes, tetralin, and naphthalene derivatives, the mid-distillate contains some fluorene derivatives and phenanthrene derivatives. The phenanthrene structure appears to be favored over that of anthracene structure (Tissot and Welte, 1978), and this appears to continue through the higher-boiling fractions of petroleum (Speight, 1994).

The five-membered heterocyclic constituents in the mid-distillate range are primarily the thiacyclane derivatives, benzothiophene derivatives, and dibenzothiophene derivatives with lesser amounts of dialkyl-, diaryl, and aryl–alkyl sulfide derivatives (Aksenova and Kayanov, 1980; Freidlina and Skorova, 1980). Alkylthiophenes are also present. As with the naphtha fractions, these sulfur species account for a minimal fraction of the total sulfur in the crude.

Although only trace amounts (usually ppm levels) of nitrogen are found in the middle distillate fractions, both neutral and basic nitrogen compounds have been isolated and identified in fractions boiling below 343°C (650°F) (Hirsch et al., 1974). Pyrrole derivatives and indole derivatives account for approximately two-thirds of the nitrogen, while the remainder is found in the basic alkylated pyridine and alkylated quinoline compounds.

The saturate constituents contribute less to the vacuum gas oil (VGO) than the aromatic constituents but more than the polar constituents that are now present at percentage rather than trace levels. Vacuum gas oil is occasionally used as a heating oil, but most commonly it is processed by catalytic cracking to produce naphtha or extraction to yield lubricating oil.

Within the vacuum gas oil, saturates, distribution of paraffins, iso-paraffins, and naphthenes are highly dependent upon the petroleum source. Generally, the naphthene constituents account for approximately two-thirds 60% of the saturate constituents, but the overall range of variation is from <20% to >80%. In most samples, the n-paraffins from C20 to C34 are still present in sufficient quantity to be detected as distinct peaks in gas chromatographic analysis.

The bulk of the saturated constituents in VGO consists of iso-paraffins and especially naphthene species, although isoprenoid compounds, such as squalane (C30) and lycopane (C40), have been detected. Analytical techniques show that the naphthenes contain from one to more than six fused rings accompanied by alkyl substitution. For mono- and diaromatics, the alkyl substitution typically involves several methyl and ethyl substituents. Hopanes and steranes have also been identified and are also used as internal markers for estimating the biodegradation of crude oils during bioremediation processes (Prince et al., 1994).

The aromatic constituents in vacuum gas oil may contain one to six fused aromatic rings that may bear additional naphthene rings and alkyl substituents in keeping with their boiling range. Mono- and diaromatics account for approximately 50% of the aromatics in petroleum vacuum gas oil samples. Analytical data show the presence of up to four fused naphthenic rings on some aromatic compounds. This is consistent with the suggestion that these species originate from the aromatization of steroids. Although present at lower concentration, alkyl benzenes and naphthelene derivatives show one long side chain and multiple short side chains.

The fused ring aromatic compounds (having three or more rings) in petroleum include phenanthrene, chrysene, and picene, as well as fluoranthene, pyrene, benzo(a)pyrene, and benzo(ghi)
perylene. The most abundant reported individual phenanthrene compounds appear to be the three derivatives. In addition, phenanthrene derivatives outnumber anthracene derivatives by as much as 100:1. In addition, chrysene derivatives are favored over pyrene derivative.

Heterocyclic constituents are significant contributors to the vacuum gas oil fraction. In terms of sulfur compounds, thiophene and thiacyclane sulfur predominate over sulfide sulfur. Some molecules even contain more than one sulfur atom. The benzothiophene derivatives and dibenzothiophene derivatives are the prevalent thiophene forms of sulfur. In the vacuum gas oil range, the nitrogen-containing compounds include higher-molecular-weight pyridine derivatives, quinoline derivatives, benzoquinoline derivatives, amide derivatives, indole derivatives, carbazole derivative, and molecules with two nitrogen atoms (diaza compounds) with three and four aromatic rings that are especially prevalent (Green et al., 1989). Typically, approximately one-third of the compounds are basic, that is, pyridine and its benzo derivatives, while the remainder is present as neutral species (amide derivatives and carbazole derivatives). Although benzo- and dibenzo-quinoline derivatives found in petroleum are rich in sterically hindered structures, hindered and unhindered structures have been found to be present at equivalent concentrations in source rocks. This has been rationalized as geochromatography in which the less polar (hindered) structures moved more readily to the reservoir and are not adsorbed on any intervening rocks structures.

Oxygen levels in the vacuum gas oil parallel the nitrogen content. Thus, the most commonly identified oxygen compounds are the carboxylic acids and phenols, collectively called naphthenic acids (Seifert and Teeter, 1970).

### 3.4.3 Vacuum Residua

The vacuum residuum (vacuum bottoms, typically 950°F or 1050°F+) is the most complex of petroleum and, in many cases, may even resemble heavy oil or extra heavy oil or tar sand bitumen in composition. Vacuum residua contain the majority of the heteroatoms originally in the petroleum and molecular weight of the constituents range up to several thousand (as near as can be determined but subject to method dependence). The fraction is so complex that the characterization of individual species is virtually impossible, no matter what claims have been made or will be made. Separation of vacuum residua by group type becomes difficult and confused because of the multi-substitution of aromatic and naphthenic species as well as of the presence of multiple functionalities in single molecules.

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

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

The nickel and vanadium that are concentrated into the vacuum residuum appear to occur in two forms: (1) porphyrins and (2) nonporphyrins (Reynolds, 1998). Because the metalloporphyrins can provide insights into petroleum maturation processes, they have been studied extensively and several families of related structures have been identified. On the other hand, the
nonporphyrin metals remain not clearly identified although some studies suggest that some of the metals in these compounds still exist in a tetra-pyrrole (porphyrin-type) environment (Pearson and Green, 1993).

It is more than likely that, in a specific residuum molecule, the heteroatoms are arranged in different functionalities, making an incredibly complex molecule. Considering how many different combinations are possible, the chances of determining every structure in a residuum are very low. Because of this seemingly insurmountable task, it may be better to determine ways of utilizing the residuum rather attempting to determine (at best questionable) molecular structures.

### 3.5 FRACTIONAL COMPOSITION

Refining petroleum involves subjecting the feedstock to a series of integrated physical and chemical unit processes (Figure 3.12) as a result of which a variety of products are generated. In some of the processes, for example, distillation, the constituents of the feedstock are isolated unchanged, whereas in other processes (such as cracking) considerable changes occur in the constituents. Feedstocks can be defined (on a relative or standard basis) in terms of three or four general fractions: asphaltenes, resins, saturates, and aromatics (Figure 3.13). Thus, it is possible to compare interlaboratory investigations and thence to apply the concept of predictability to refining sequences and potential products. Recognition that refinery behavior is related to the composition of the feedstock has led to a multiplicity of attempts to establish petroleum and its fractions as compositions of matter. As a result, various analytical techniques have been developed for the identification and quantification of every molecule in the lower-boiling fractions of petroleum. It is now generally recognized that the name petroleum does not describe a composition of matter but rather a mixture of various organic compounds that includes a wide range of molecular weights and molecular types that exist in balance with each other (Speight, 1994; Long and Speight, 1998). There must also be some questions of the advisability (perhaps futility is a better word) of attempting to describe every molecule in petroleum. The true focus should be to what ends these molecules can be used.

The fractionation methods available to the petroleum industry allow a reasonably effective degree of separation of hydrocarbon mixtures (Speight, 2014, 2015). 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.

It is more generally true, however, that the success of any attempted fractionation procedure involves not only the application of one particular technique but also the utilization of several integrated techniques, especially those techniques involving the use of chemical and physical properties to differentiate among the various constituents. For example, the standard processes of physical fractionation used in the petroleum industry are those of distillation and solvent treatment, as well as adsorption by surface-active materials. Chemical procedures depend on specific reactions, such as the interaction of olefins with sulfuric acid or the various classes of adduct formation. Chemical fractionation is often but not always successful because of the complex nature of crude oil. This may result in unprovoked chemical reactions that have an adverse effect on the fractionation and the resulting data. Indeed, caution is advised when using methods that involve chemical separation of the constituents.

The order in which the several fractionation methods are used is determined not only by the nature and/or composition of the crude oil but also by the effectiveness of a particular process and its compatibility with the other separation procedures to be employed. Thus, although there are wide variations in the nature of refinery feedstocks, there have been many attempts to devise standard methods of petroleum fractionation. However, the various laboratories are inclined to adhere firmly to, and promote, their own particular methods. Recognition that no one particular method may satisfy all the requirements of petroleum fractionation is the first step in any fractionation study. This is due, in the main part, to the complexity of petroleum not only from the
distribution of the hydrocarbon species but also from the distribution of the heteroatom (nitrogen, oxygen, and sulfur) species.

### 3.5.1 Solvent Methods

Fractionation of petroleum by distillation is an excellent means by which the volatile constituents can be isolated and studied. However, the nonvolatile residuum, which may actually constitute from
Feedstock Composition

1% to 60% of the petroleum, cannot be fractionated by distillation without the possibility of thermal decomposition, and as a result, alternative methods of fractionation have been developed.

The distillation process separates light (lower-molecular-weight) and heavy (higher-molecular-weight) constituents by virtue of their volatility and involves the participation of a vapor phase and a liquid phase. These are, however, physical processes that involve the use of two liquid phases, usually a solvent phase and an oil phase.

Solvent methods have also been applied to petroleum fractionation on the basis of molecular weight. The major molecular weight separation process used in the laboratory as well as in the refinery is solvent precipitation. Solvent precipitation occurs in a refinery in a deasphalting unit (Figure 3.14) and is essentially an extension of the procedure for separation by molecular weight, although some separation by polarity might also be operative. The deasphalting process is usually applied to the higher-molecular-weight fractions of petroleum such as atmospheric and vacuum residua.

These fractionation techniques can also be applied to cracked residua, asphalt, bitumen, and even to virgin petroleum, but in the last case the possibility of losses of the lower-boiling constituents is apparent; hence, the recommended procedure for virgin petroleum is, first, distillation followed by fractionation of the residua.

The simplest application of solvent extraction consists of mixing petroleum with another liquid, which results in the formation of two phases. This causes distribution of the petroleum constituents over the two phases; the dissolved portion (the extract) and the nondissolved portion (the raffinate).

The ratio of the concentration of any particular component in the two phases is known as the distribution coefficient \( K \):

\[
K = \frac{C_1}{C_2}
\]

where \( C_1 \) and \( C_2 \) are the concentrations of the components in the various phases. The distribution coefficient is usually constant and may vary only slightly, if at all, with the concentration of the other components. In fact, the distribution coefficients may differ for the various components of the mixture to such an extent that the ratio of the concentrations of the various components in the

![Figure 3.13 Separation scheme for various feedstocks.](image-url)
solvent phase differs from that in the original petroleum; this is the basis for solvent extraction procedures.

It is generally molecular type, not molecular size, which is responsible for the solubility of species in various solvents. Thus, solvent extraction separates petroleum fractions according to type, although within any particular series there is a separation according to molecular size. Lower-molecular-weight hydrocarbons of a series (the light fraction) may well be separated from their higher-molecular-weight homologues (the heavy fraction) by solvent extraction procedures.

In general, it is advisable that selective extraction be employed with fairly narrow boiling range fractions. However, the separation achieved after one treatment with the solvent is rarely complete, and several repetitions of the treatment are required. Such repetitious treatments are normally carried out by the movement of the liquids countercurrently through the extraction equipment (countercurrent extraction), which affords better yields of the extractable materials.

The list of compounds that have been suggested as selective solvents for the preferential extraction fractionation of petroleum contains a large selection of different functional types (Table 3.5). However, before any extraction process is attempted, it is necessary to consider the following criteria: (1) the differences in the solubility of the petroleum constituents in the solvent should be substantial, (2) the solvent should be significantly less dense or denser than the petroleum (product) to be separated to allow easier countercurrent flow of the two phases, and (3) separation of the solvent from the extracted material should be relatively easy.

It may also be advantageous to consider other properties, such as viscosity, surface tension, and the like, as well as the optimal temperature for the extraction process. Thus, aromatics can be

**FIGURE 3.14** Placement of a deasphalting unit in the refinery (see also Figure 3.12).
separated from naphthene and paraffinic hydrocarbons by the use of selective solvents. Furthermore, aromatics with differing numbers of aromatic rings that may exist in various narrow boiling fractions can also be effectively separated by solvent treatment.

The separation of crude oil into two fractions—(1) the asphaltene fraction and (2) the maltene fraction—is conveniently brought about by the use of low-molecular-weight paraffinic hydrocarbons, which were recognized to have selective solvency for hydrocarbons, and simply relatively low-molecular-weight hydrocarbon derivatives. The more complex, the higher the molecular weight value of compounds that are precipitated particularly well by the addition of 40 volumes of \( n \)-pentane or \( n \)-heptane in the methods generally preferred at present (Speight et al., 1984; Speight, 1994) although hexane is used occasionally (Yan et al., 1997). It is no doubt that there is a separation of the chemical components with the most complex structures from the mixture, and this fraction, which should correctly be called “\( n \)-pentane asphaltenes” or “\( n \)-heptane asphaltenes,” is qualitatively and quantitatively reproducible (Figure 3.13).

Variation in the solvent type also causes significant changes in asphaltene yield. For example, in the ease of a Western Canadian bitumen and, indeed, for conventional crude oils, branched-chain paraffins or terminal olefins do not precipitate the same amount of asphaltenes as do the corresponding normal paraffins (Mitchell and Speight, 1973). Cycloparaffin derivatives (naphthene derivatives) have a remarkable effect on asphaltene yield and give results totally unrelated to those from any other nonaromatic solvent. For example, when cyclopentane, cyclohexane, or their methyl derivatives are employed as precipitating media, only approximately 1% w/w of the material remains insoluble.

To explain those differences, it was necessary to consider the solvent power of the precipitating liquid, which can be related to molecular properties (Hildebrand et al., 1970). The solvent power

<table>
<thead>
<tr>
<th>TABLE 3.5 Compound Types Used for the Selective Extraction of Petroleum</th>
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</thead>
<tbody>
<tr>
<td><strong>Esters</strong></td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
</tr>
<tr>
<td><strong>Aldehydes</strong></td>
</tr>
<tr>
<td><strong>Acids</strong></td>
</tr>
<tr>
<td><strong>Ketones</strong></td>
</tr>
<tr>
<td><strong>Amines</strong></td>
</tr>
<tr>
<td><strong>Amides</strong></td>
</tr>
<tr>
<td><strong>Nitrocompounds</strong></td>
</tr>
<tr>
<td><strong>Nitriles</strong></td>
</tr>
</tbody>
</table>

*Note: R and R’ are alkyl aromatic radicals, and if both are alkyl or both are aromatic they may or may not be the same.*
of nonpolar solvents has been expressed as a solubility parameter ($\delta$) and equated to the internal pressure of the solvent, that is, the ratio between the surface tension ($\gamma$) and the cubic root of the molar volume ($V$):

$$\delta_1 = \frac{\gamma}{\sqrt[3]{V}}$$

Alternatively, the solubility parameter of nonpolar solvents can be related to the energy or vaporization $\Delta R^\nu$ and the molar volume:

$$\delta_2 = \left(\frac{\Delta R^\nu}{V}\right)^{1/2}$$

Also

$$\delta_2 = \left(\frac{\Delta H^\nu - RT}{V}\right)^{1/2}$$

where

- $\Delta H^\nu$ is the heat of vaporization
- $R$ is the gas constant
- $T$ is the absolute temperature

The introduction of a polar group (heteroatom function) into the molecule of the solvent has significant effects on the quantity of precipitate. For example, treatment of a residuum with a variety of ethers or treatment of asphaltenes with a variety of solvents illustrates this point (Speight, 1979). In the latter instance, it was not possible to obtain data from addition of the solvent to the whole feedstock per se since the majority of the nonhydrocarbon materials were not miscible with the feedstock. It is nevertheless interesting that, as with the hydrocarbons, the amount of precipitate, or asphaltene solubility, can be related to the solubility parameter.

The solubility parameter allows an explanation of certain apparent anomalies, for example, the insolubility of asphaltenes in pentane and the near complete solubility of the materials in cyclopentane. Moreover, the solvent power of various solvents is in agreement with the derivation of the solubility parameter; for any one series of solvents, the relationship between the amount of precipitate (or asphaltene solubility) and the solubility parameter $\delta$ is quite regular.

In any method used to isolate asphaltenes as a separate fraction, standardization of the technique is essential. For many years, the method of asphaltenes separation was not standardized, and even now it remains subject to the preferences of the standard organizations of different countries. The use of both $n$-pentane and $n$-heptane has been widely advocated, and although $n$-heptane is becoming the deasphalting liquid of choice, this is by no means a hard-and-fast rule. And it must be recognized that large volumes of solvent may be required to effect a reproducible separation, similar to amounts required for consistent asphaltene separation. It is also preferable that the solvents be of sufficiently low boiling point that complete removal of the solvent from the fraction can be effected and, most important, the solvent must not react with the feedstock. Hence, the preference for the use of hydrocarbon liquids in standard methods, although the several standard methods that have been used are not unanimous in the ratio of hydrocarbon liquid to feedstock.

<table>
<thead>
<tr>
<th>Method</th>
<th>Deasphalting Liquid</th>
<th>Volume (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D893 (2015)</td>
<td>$n$-Pentane</td>
<td>10</td>
</tr>
<tr>
<td>ASTM D2007 (2015)</td>
<td>$n$-Pentane</td>
<td>10</td>
</tr>
<tr>
<td>ASTM D3279 (2015)</td>
<td>$n$-Heptane</td>
<td>100</td>
</tr>
<tr>
<td>ASTM D4124 (2015)</td>
<td>$n$-Heptane</td>
<td>100</td>
</tr>
</tbody>
</table>
Feedstock Composition

However, it must be recognized that some of these methods were developed for use with feedstocks other than heavy oil and adjustments are necessary.

Although \( n \)-pentane and \( n \)-heptane are the solvents of choice in the laboratory, other solvents can be used (Speight, 1979) and cause the separation of asphaltenes as brown-to-black powdery materials. In the refinery, supercritical low-molecular-weight hydrocarbons (e.g., liquid propane, liquid butane, or mixtures of both) are the solvents of choice and the product is a semisolid (tacky) to solid asphalt. The amount of asphalt that settles out of the paraffin/residuum mixture depends on the size of the paraffin, the temperature, and the paraffin-to-feedstock ratio (Corbett and Petrossi, 1978; Speight et al., 1984; Speight, 2014, 2015).

Insofar as industrial solvents are very rarely one compound, it was also of interest to note that the physical characteristics of two different solvent types, in this case benzene and \( n \)-pentane, are additive on a mole-fraction basis (Mitchell and Speight, 1973) and also explain the variation of solubility with temperature. The data also show the effects of blending a solvent with the bitumen itself and allowing the resulting solvent–heavy oil blend to control the degree of bitumen solubility. Varying proportions of the hydrocarbon alter the physical characteristics of the oil to such an extent that the amount of precipitate (asphaltenes) can be varied accordingly within a certain range.

At constant temperature, the quantity of precipitate first increases with the increasing ratio of solvent to feedstock and then reaches a maximum (Speight et al., 1984). In fact, there are indications that when the proportion of solvent in the mix is <35% little or no asphaltenes are precipitated. In addition, when pentane and the lower-molecular-weight hydrocarbon solvents are used in large excess, the quantity of precipitate and the composition of the precipitate change with increasing temperature (Mitchell and Speight, 1973).

Contact time between the hydrocarbon and the feedstock also plays an important role in asphaltene separation (Speight et al., 1984). Yields of the asphaltenes reach a maximum after approximately 8 hours, which may be ascribed to the time required for the asphaltene particles to agglomerate into particles of a filterable size as well as the diffusion-controlled nature of the process. Heavier feedstocks also need time for the hydrocarbon to penetrate their mass.

After removal of the asphaltene fraction, further fractionation of petroleum is also possible by variation of the hydrocarbon solvent. For example, liquefied gases, such as propane and butane, precipitate as much as 50% by weight of the residuum or bitumen. The precipitate is a black, tacky, semisolid material, in contrast to the pentane-precipitated asphaltenes, which are usually brown, amorphous solids. Treatment of the propane precipitate with pentane then yields the insoluble brown, amorphous asphaltenes and soluble, near-black, semisolid resins, which are, as near as can be determined, equivalent to the resins isolated by adsorption techniques (Speight, 2014, 2015).

### 3.5.2 Adsorption Methods

Separation by adsorption chromatography essentially commences with the preparation of a porous bed of finely divided solid, the adsorbent. The adsorbent is usually contained in an open tube (column chromatography); the sample is introduced at one end of the adsorbent bed and induced to flow through the bed by means of a suitable solvent. As the sample moves through the bed, the various components are held (adsorbed) to a greater or lesser extent depending on the chemical nature of the component. Thus, those molecules that are strongly adsorbed spend considerable time on the adsorbent surface rather than in the moving (solvent) phase, but components that are slightly adsorbed move through the bed comparatively rapidly.

It is essential that, before the application of the adsorption technique to the petroleum, the asphaltenes first be completely removed, for example, by any of the methods outlined in the previous section. The prior removal of the asphaltenes is essential insofar as they are usually difficult to remove from the earth or clay and may actually be irreversibly adsorbed on the adsorbent.

By definition, the *saturate fraction* consists of paraffins and cycloparaffin derivatives (naphthene derivatives). The single-ring naphthene derivatives, or cycloparaffin derivatives, present in
petroleum are primarily alkyl-substituted cyclopentane and cyclohexane rings. The alkyl groups are usually quite short, with methyl, ethyl, and isopropyl groups the predominant substituents. As the molecular weight of the naphthenes increases, the naphthene fraction contains more condensed rings with six-membered rings predominating. However, five-membered rings are still present in the complex higher-molecular-weight molecules.

The aromatic fraction consists of those compounds containing an aromatic ring and varies from monoaromatics (containing one benzene ring in a molecule) to diaromatics (substituted naphthalene) to triaromatics (substituted phenanthrene). Higher condensed ring systems (tetra-aromatics, penta-aromatics) are also known but are somewhat less prevalent than the lower ring systems, and each aromatic type will have increasing amounts of condensed ring naphthene attached to the aromatic ring as molecular weight is increased.

However, depending upon the adsorbent employed for the separation, a compound having an aromatic ring (i.e., six-carbon aromatic atoms) carrying side chains consisting in toto of more than six-carbon atoms (i.e., more than six-carbon nonaromatic atoms) will appear in the aromatic fraction.

Careful monitoring of the experimental procedures and the nature of the adsorbent has been responsible for the successes achieved with this particular technique. Early procedures consisted of warming solutions of the petroleum fraction with the adsorbent and subsequent filtration. This procedure has continued to the present day, and separation by adsorption is used commercially in plant operations in the form of clay treatment of crude oil fractions and products. In addition, the proportions of each fraction are subject to the ratio of adsorbent to deasphaltened oil.

It is also advisable, once a procedure using a specific adsorbent has been established, that the same type of adsorbent be employed for future fractionation since the ratio of the product fractions varies from adsorbent to adsorbent. It is also very necessary that the procedure be used with caution and that the method not only be reproducible but quantitative recoveries be guaranteed; reproducibility with only, say, 85% of the material recoverable is not a criterion of success.

There are two procedures that have received considerable attention over the years and these are (1) the method by the U.S. Bureau of Mines—American Petroleum Institute (USBM-API) method and (2) the saturates–aromatics–resin constituents–asphaltene constituents (SARA) method. This latter method is often also called the saturates–aromatics–polar constituents–asphaltene constituents (SAPA) method. These two methods are used as representing the standard methods of petroleum fractionation. Other methods are also noted, especially when the method has added further meaningful knowledge to compositional studies (Speight, 2014, 2015).

However, there are precautions that must be taken when attempting to separate heavy feedstocks (heavy oil, tar sand bitumen) or polar feedstocks into constituent fractions. The disadvantages in using ill-defined adsorbents are that adsorbent performance differs with the same feed and, in certain instances, may even cause chemical and physical modification of the feed constituents. The use of a chemical reactant like sulfuric acid should only be advocated with caution since feedstocks react differently and may even cause irreversible chemical changes and/or emulsion formation (Abdel-Aal et al., 2016). These advantages may be of little consequence when it is not, for various reasons, the intention to recover the various product fractions in toto or in the original state, but in terms of the compositional evaluation of different feedstocks the disadvantages are very real.

In summary, the terminology used for the identification of the various methods might differ. However, in general terms, group-type analysis of petroleum is often identified by the acronyms for the names: PONA (paraffins, olefins, naphthenes, and aromatics), PIONA (paraffins, iso-paraffins, olefins, naphthenes, and aromatics), PNA (paraffins, naphthenes, and aromatics), PINA (paraffins, iso-paraffins, naphthenes, and aromatics), or SARA (saturates, aromatics, resins, and asphaltenes). However, it must be recognized that the fractions produced by the use of different adsorbents will differ in content and will also be different from fractions produced by solvent separation techniques.

The variety of fractions isolated by these methods and the potential for the differences in composition of the fractions makes it even more essential that the method is described accurately and that it is reproducible not only in any one laboratory but also between various laboratories.
3.5.3 Chemical Methods

Methods of fractionation using chemical reactants are entirely different in nature from the methods described in the preceding sections. Although several methods using chemical reactants have been applied to fractionation, methods such as adsorption, solvent treatment, and treatment with alkali (Speight, 2014, 2015) are often applied to product purification as well as separation.

The method of chemical separation commonly applied to separate crude oil into various fractions is treatment with sulfuric acid and since this method has also been applied in the refinery but with limited success in the fractionation of heavy oil and/or bitumen due to the formation of complex sulfates and difficult-to-break emulsions (Speight, 2014, 2015). Obviously, the success of this fractionation method is feedstock dependent and, in conclusion, it would appear that the test be left more as a method of product cleaning for which it was originally designed rather than a method of separation of the various fractions.

3.6 USE OF THE DATA

In the simplest sense, crude oil is a composite of four major fractions that are defined by the method of separation (Figure 3.13) (Speight, 2014, 2015), but, more important, the behavior and properties of any feedstock are dictated by composition (Speight, 2014, 2015). Although early studies were primarily focused on the composition and behavior of asphalt, the techniques developed for those investigations have provided an excellent means of studying heavy feedstocks (Tissot, 1984). Later studies have focused not only on the composition of petroleum and its major operational fractions but on further fractionation that allows different feedstocks to be compared on a relative basis and to provide a very simple but convenient feedstock map.

Such a map does not give any indication of the complex interrelationships of the various fractions (Koots and Speight, 1975), although predictions of feedstock behavior are possible using such data. It is necessary to take the composition studies one step further using subfractionation of the major fractions to obtain a more representative indication of petroleum composition.

Thus, by careful selection of an appropriate technique, it is possible to obtain an overview of petroleum composition that can be used for behavioral predictions. By taking the approach one step further and by assiduous collection of various subfractions from the original bulk fractions (Figure 3.13), it becomes possible to develop the petroleum map and add an extra dimension to compositional studies (Figure 3.15). Petroleum and heavy feedstocks then appear more as a continuum than as four specific fractions. Such a concept has also been applied to the asphaltene fraction of petroleum in which asphaltenes are considered a complex state of matter based on molecular weight and polarity (Long, 1979, 1981; Speight, 1994).

Furthermore, petroleum can be viewed as consisting of two continuous distributions, one of molecular weight and the other of molecular type. Using data from molecular weight studies and elemental analyses, the number of nitrogen and sulfur atoms in the aromatic fraction and in the polar aromatic fraction can also be exhibited. These data showed that not only can every molecule in the resins and asphaltenes has more than one sulfur atom or more than one nitrogen atom but also some molecules probably contain both sulfur and nitrogen. As the molecular weight of the aromatic fraction decreases, the sulfur and nitrogen contents of the fractions also decrease. In contrast to the sulfur-containing molecules, which appear in both the naphthene aromatics and the polar aromatic fractions, the oxygen compounds present in the heavy fractions of petroleum are normally found in the polar aromatics fraction.

More recent work (Long and Speight, 1989) involved the development of a different type of compositional map using the molecular weight distribution and the molecular type distribution as coordinates. The separation involved the use of an adsorbent such as clay, and the fractions were characterized by solubility parameter as a measure of the polarity of the molecular types. The molecular weight distribution can be determined by gel permeation chromatography. Using these
two distributions, a map of composition can be prepared using molecular weight and solubility parameter as the coordinates for plotting the two distributions. Such a composition map can provide insights into many separation and conversion processes used in petroleum refining.

The molecular type was characterized by the polarity of the molecules, as measured by the increasing adsorption strength on an adsorbent. At the time of the original concept, it was unclear how to characterize the continuum in molecular type or polarity. For this reason, the molecular type coordinate of their first maps was the yield of the molecular types ranked in order of increasing polarity. However, this type of map can be somewhat misleading because the areas are not related to the amounts of material in a given type. The horizontal distance on the plot is a measure of the yield, and there is not a continuous variation in polarity for the horizontal coordinate. It was suggested that the solubility parameter of the different fractions could be used to characterize both polarity and adsorption strength.

In order to attempt to remove some of these potential ambiguities, more recent developments of this concept have focused on the solubility parameter, estimated by the values for the eluting solvents that remove the fractions from the adsorbent. The simplest maps that can be derived using the solubility parameter are produced with the solubility parameters of the solvents used in solvent separation procedures and equating these parameters to the various fractions (Figure 3.16).

Thus, a composition 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, is shown for various regions on the map for a sample of atmospheric residuum (Figure 3.17)
**FIGURE 3.16** A petroleum map based on molecular weight and solubility parameter.

**FIGURE 3.17** Property prediction using a petroleum map.
The plot shows molecular weight plotted against weight percent yield in order of increasing polarity. The dashed line is the envelope of composition of the total sample. The slanted lines show the boundaries of solvent-precipitated fractions, and the vertical lines show the boundaries of the fractions obtained by clay adsorption of the pentane-deasphalted oil. A composition map can be very useful for predicting the effectiveness of various types of separations or conversions of petroleum (Figure 3.18) (Long and Speight, 1998). These processes are adsorption, distillation, solvent precipitation with relatively nonpolar solvents, and solvent extraction.

A composition map can be very useful for predicting the effectiveness of various types of separations or conversions of petroleum (Figure 3.18) (Long and Speight, 1998). These processes are adsorption, distillation, solvent precipitation with relatively nonpolar solvents, and solvent extraction.
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with polar solvents. The vertical lines show the cut points between saturates aromatics and polar aromatics as determined by clay chromatography. The slanted lines show how distillation, extraction, and solvent precipitation can divide the composition map. The line for distillation divides the map into distillate, which lies below the dividing line, and bottoms, which lies above the line. As the boiling point of the distillate is raised, the line moves upward, including higher-molecular-weight materials and more of the polar species in the distillate and rejecting lower-molecular-weight materials from the bottoms. As more of the polar species are included in the distillate, the carbon residue of the distillate rises. In contrast to the cut lines generated by separation processes, conversion processes move materials in the composition from one molecular type to another (Figure 3.19) (Long and Speight, 1998).

The ultimate decision in the choice of any particular fractionation technique must be influenced by the need for the data. For example, there are those needs that require only that the crude oil be separated into four bulk fractions. On the other hand, there may be the need to separate the crude oil into many subfractions in order to define specific compound types (Green et al., 1988; Vogh and Reynolds, 1988). Neither method is incorrect; each method is merely being used to answer the relevant questions about the character of the crude oil.

REFERENCES


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