CHAPTER

2

PETROLEUM AND PETROLEUM PRODUCTS

2.1. PETROLEUM

Petroleum is a naturally occurring mixture of hydrocarbons, generally in a liquid state, that may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements (ASTM D-4175). Consequently, it is not surprising that petroleum can vary in composition properties and produce wide variations in refining behavior as well as product properties.

Petroleum being processed in refineries is becoming increasingly heavier (higher amounts of residuum) and higher sulfur content) (Speight, 1999, and references cited therein). Market demand (market pull) dictates that residua must be upgraded to higher-value products (Speight and Ozum, 2002). In short, the value of petroleum depends on its quality for refining and whether or not a product slate can be obtained to fit market demand.

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

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

Sulfur reduction processes are sensitive to both amount and structure of the sulfur compounds being removed. Tests that can provide information about both of these factors are becoming increasingly important, and analytical tests that provide information about other constituents of interest (e.g., nitrogen, organometallic constituents) are also valuable and being used for characterization.
But before delving into the detailed aspects of petroleum product analysis, it is necessary to understand the nature and character of petroleum as well as the methods used to produce petroleum products. This will present to the reader the background that is necessary to understand petroleum and the processes used to convert it to products. The details of the chemistry are not presented here and can be found elsewhere (Speight, 1999, 2000; Speight and Ozum, 2002).

Thus it is the intent of this chapter to present an overview with some degree of detail of the character of petroleum and the methods used to produce products. The character of petroleum will be presented, for the purposes of this chapter, by application of various analytical methods.

Sections relating to natural gas (a constituent of petroleum), natural gas liquids, and natural gasoline are also included.

### 2.1.1. Definitions

Petroleum (also called *crude oil*) is a naturally mixture of hydrocarbons, generally in the liquid state, that may also include compounds of sulfur, nitrogen, oxygen, and metals and other elements (ASTM D-4175; Speight, 2001 and references cited therein). Inorganic sediment and water may also be present. Thus, for the purposes of this text, a petroleum product is any product that is manufactured during petroleum refining and, as a consequence, petrochemical products are not included in this definition or in this text.

Attempts have been made to define or classify petroleum based on various distillation properties when combined with another property such as density. It has been suggested that a crude should be called asphaltic if the distillation residue contained less than 2% wax and paraffinic if it contained more than 5%. A division according to the chemical composition of the 250–300°C (480–570°F) fraction has also been suggested (Table 2.1).

<table>
<thead>
<tr>
<th>Composition of 250–300°C (480–570°F) Fraction</th>
<th>Crude oil Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic</td>
<td>Naphthenic</td>
</tr>
<tr>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>&gt;46, &lt;61</td>
<td>&gt;22, &lt;32</td>
</tr>
<tr>
<td>&gt;42, &lt;45</td>
<td>&gt;38, &lt;39</td>
</tr>
<tr>
<td>&gt;15, &lt;26</td>
<td>&gt;61, &lt;76</td>
</tr>
<tr>
<td>&gt;27, &lt;35</td>
<td>&gt;36, &lt;47</td>
</tr>
<tr>
<td>&gt;8</td>
<td>&gt;57, &lt;78</td>
</tr>
</tbody>
</table>
Difficulties arise in using such a classification in that in the fractions boiling above 200°C (390°F) the molecules can no longer be placed in one group because most of them are of a typically mixed nature. Purely naphthenic or aromatic molecules occur very seldom; cyclic compounds generally contain paraffinic side chains and often even aromatic and naphthenic rings side by side. More direct chemical information is often desirable and can be supplied by means of the correlation index (CI).

The correlation index is based on the plot of specific gravity versus the reciprocal of the boiling point in degrees Kelvin ($\circ K = \circ C + 273$). For pure hydrocarbons, the line described by the constants of the individual members of the normal paraffin series is given a value of CI = 0 and a parallel line passing through the point for the values of benzene is given as CI = 100 (Fig. 2.1); thus,

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

Figure 2.1. Reference data for the correlation index (from Speight, 1999)
where $d$ is the specific gravity and $K$ is the average boiling point of the petroleum fraction as determined by the standard distillation method (ASTM D-86, ASTM D-1160).

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

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

Another derived number, the UOP characterization factor, is also a widely used method for defining petroleum; the Characterization Factor is derived from the formula:

$$K = 3\sqrt{T_B/d}$$

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

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

The underlying premise for these methods of definition or classification is uniformity of the molecular nature of the feedstocks. This is not in fact
the case, and when blends are employed as refinery feedstocks, the methods do not take into account any potential interactions between the constituents of each member of the blend.

The most adequate definitions of petroleum come from legal documents, where petroleum is defined directly or by inference (Speight, 1999, 2000).

2.1.2. Composition

In all of these attempts at a definition or classification of petroleum, it must be remembered that petroleum exhibits wide variations in composition and properties, and these variations not only occur in petroleum from different fields but may also be manifested in petroleum taken from different production depths in the same well. The mixture of hydrocarbons is highly complex. Paraffinic, naphthenic, and aromatic structures can occur in the same molecule, and the complexity increases with boiling range of the petroleum fraction. In addition, petroleum varies in physical appearance from a light-colored liquid to the more viscous heavy oil. The near-solid or solid bitumen that occurs in tar sand deposits is different from petroleum and heavy oil, as evidenced by the respective methods of recovery (Speight, 1999, 2000).

Elemental analysis of petroleum shows that the major constituents are carbon and hydrogen with smaller amounts of sulfur (0.1–8% w/w), nitrogen (0.1–1.0% w/w), and oxygen (0.1–3% w/w), and trace elements such as vanadium, nickel, iron, and copper present at the part per million (ppm) level. Of the non-hydrocarbon (heteroelements) elements, sulfur is the most abundant and often considered the most important by refiners. However, nitrogen and the trace metals also have deleterious effects on refinery catalysts and should not be discounted because of relative abundance. Process units with, for example, a capacity of 50,000 bbl/day that are in operation continuously can soon reflect the presence of the trace elements. The effect of oxygen, which also has an effect on refining catalysts, has received somewhat less study than the other heteroelements but remains equally important in refining.

Petroleum suitability for refining (to produce a slate of predetermined products) (Table 2.2) is determined by application of a series of analytical methods (Speight, 2001) that provide information that is sufficient to assess the potential quality of the petroleum as a feedstock and also to indicate whether any difficulties might arise in handling, refining, or transportation. Such information may be obtained either by (1) a preliminary assay of petroleum or (2) a full assay of petroleum that involves presentation of a true boiling point curve and the analysis of fractions throughout the full range of petroleum.
Table 2.2. General Summary of Product Types and Distillation Range

<table>
<thead>
<tr>
<th>Product</th>
<th>Lower Carbon Limit</th>
<th>Upper Carbon Limit</th>
<th>Lower Boiling Point °C</th>
<th>Upper Boiling Point °C</th>
<th>Lower Boiling Point °F</th>
<th>Upper Boiling Point °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery gas</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>161</td>
<td>-1</td>
<td>-259</td>
<td>31</td>
</tr>
<tr>
<td>Liquefied petroleum gas</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-42</td>
<td>-1</td>
<td>-44</td>
<td>31</td>
</tr>
<tr>
<td>Naphtha</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>C&lt;sub&gt;17&lt;/sub&gt;</td>
<td>36</td>
<td>302</td>
<td>97</td>
<td>575</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>-1</td>
<td>216</td>
<td>31</td>
<td>421</td>
</tr>
<tr>
<td>Kerosene/diesel fuel</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>126</td>
<td>258</td>
<td>302</td>
<td>575</td>
</tr>
<tr>
<td>Aviation turbine fuel</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;</td>
<td>126</td>
<td>287</td>
<td>302</td>
<td>548</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>216</td>
<td>421</td>
<td>&gt;343</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wax</td>
<td>C&lt;sub&gt;17&lt;/sub&gt;</td>
<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>302</td>
<td>&gt;343</td>
<td>575</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Asphalt</td>
<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>&gt;C&lt;sub&gt;50&lt;/sub&gt;*</td>
<td>&gt;1000*</td>
<td>&gt;1832*</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.

2.2. PETROLEUM ASSAY

An efficient assay is derived from a series of test data that give an accurate description of petroleum quality and allow an indication of its behavior during refining. The first step is, of course, to ensure adequate (correct) sampling by use of the prescribed protocols (ASTM D-4057).

Thus analyses are performed to determine whether each batch of crude oil received at the refinery is suitable for refining purposes. The tests are also applied to determine whether there has been any contamination during wellhead recovery, storage, or transportation that may increase the processing difficulty (cost). The information required is generally crude oil dependent or specific to a particular refinery and is also a function of refinery operations and desired product slate.

To obtain the necessary information, two different analytical schemes are commonly used. These are (1) an inspection assay and (2) a comprehensive assay.

Inspection assays usually involve determination of several key bulk properties of petroleum (e.g., API gravity, sulfur content, pour point, and distillation range) as a means of determining whether major changes in characteristics have occurred since the last comprehensive assay was performed.

For example, a more detailed inspection assay might consist of the following tests: API gravity (or density or relative density), sulfur content, pour point, viscosity, salt content, water and sediment content, trace metals
(or organic halides). The results from these tests with the archived data from a comprehensive assay provide an estimate of any changes that have occurred in the crude oil that may be critical to refinery operations. Inspection assays are routinely performed on all crude oils received at a refinery.

On the other hand, the comprehensive (or full) assay is more complex (as well as time-consuming and costly) and is usually only performed only when a new field comes on stream, or when the inspection assay indicates that significant changes in the composition of the crude oil have occurred. Except for these circumstances, a comprehensive assay of a particular crude oil stream may not (unfortunately) be updated for several years.

In this section, as in others throughout this book, no preference is given to any particular tests. All lists of tests are alphabetical.

### 2.2.1. Carbon Residue, Asphaltene Content

The carbon residues of petroleum and petroleum products serve as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat.

Tests for Conradson carbon residue (ASTM D-189, IP 13), Ramsbottom carbon residue (ASTM D-524, IP 14), the microcarbon carbon residue (ASTM D4530, IP 398), and asphaltene content (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) are sometimes included in inspection data on petroleum. The data give an indication of the amount of coke that will be formed during thermal processes as well as an indication of the amount of high-boiling constituents in petroleum.

The determination of the carbon residue of petroleum or a petroleum product is applicable to relatively nonvolatile samples that decompose on distillation at atmospheric pressure. Samples that contain ash-forming constituents will have an erroneously high carbon residue, depending on the amount of ash formed. All three methods are applicable to relatively nonvolatile petroleum products that partially decompose on distillation at atmospheric pressure. Crude oils having a low carbon residue may be distilled to a specified residue with the carbon residue test of choice then applied to that residue.

In the Conradson carbon residue test (ASTM D-189, IP 13), a weighed quantity of sample is placed in a crucible and subjected to destructive distillation for a fixed period of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccator and weighed and the residue is reported as a percentage (% w/w) of the original sample (Conradson carbon residue).

In the Ramsbottom carbon residue test (ASTM Test Method D524, IP 14), the sample is weighed into a glass bulb that has a capillary opening and
is placed into a furnace (at 550°C, 1022°F). The volatile matter is distilled from the bulb and the nonvolatile matter that remains in the bulb decomposes to form thermal coke. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and weighed to report the residue (Ramsbottom carbon residue) as a percentage (% w/w) of the original sample.

In the microcarbon residue test (ASTM D4530, IP 398), a weighed quantity of the sample placed in a glass vial is heated to 500°C (932°F) under an inert (nitrogen) atmosphere in a controlled manner for a specific time and the carbonaceous residue [carbon residue (micro)] is reported as a percentage (% w/w) of the original sample.

The data produced by the microcarbon test (ASTM D4530, IP 398) are equivalent to those by the Conradson carbon residue method (ASTM D-189 IP 13). However, this microcarbon test method offers better control of test conditions and requires a smaller sample. Up to 12 samples can be run simultaneously. This test method is applicable to petroleum and to petroleum products that partially decompose on distillation at atmospheric pressure and is applicable to a variety of samples that generate a range of yields (0.01% w/w to 30% w/w) of thermal coke.

As noted, in any of the carbon residue tests, ash-forming constituents (ASTM D-482) or nonvolatile additives present in the sample will be included in the total carbon residue reported, leading to higher carbon residue values and erroneous conclusions about the coke-forming propensity of the sample.

The asphaltene fraction (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) is the highest-molecular-weight, most complex fraction in petroleum. The asphaltene content gives an indication of the amount of coke that can be expected during processing (Speight, 1999; Speight, 2001, Speight and Ozum 2002).

In any of the methods for the determination of the asphaltene content, the crude oil or product (such as asphalt) is mixed with a large excess (usually >30 volumes hydrocarbon per volume of sample) of low-boiling hydrocarbon such as n-pentane or n-heptane. For an extremely viscous sample, a solvent such as toluene may be used before the addition of the low-boiling hydrocarbon but an additional amount of the hydrocarbon (usually >30 volumes hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage (% w/w) of the original sample.

It must be recognized that, in any of these tests, different hydrocarbons (such as n-pentane or n-heptane) will give different yields of the asphaltene fraction and if the presence of the solvent is not compensated for by use of additional hydrocarbon the yield will be erroneous. In addition, if the
hydrocarbon is not present in large excess, the yields of the asphaltene fraction will vary and will be erroneous (Speight, 1999).

The precipitation number is often equated to the asphaltene content, but there are several issues that remain obvious in its rejection for this purpose. For example, the method used to determine the precipitation number (ASTM D-91) advocates the use of naphtha for use with black oil or lubricating oil and the amount of insoluble material (as a % v/v of the sample) is the precipitation number. In the test, 10 ml of sample is mixed with 90 ml of ASTM precipitation naphtha (which may or may nor have a constant chemical composition) in a graduated centrifuge cone and centrifuged for 10 min at 600–700 rpm. The volume of material on the bottom of the centrifuge cone is noted until repeat centrifugation gives a value within 0.1 ml (the precipitation number). Obviously, this can be substantially different from the asphaltene content.

2.2.2. Density (Specific Gravity)

For clarification, it is necessary to understand the basic definitions that are used: (1) density is the mass of liquid per unit volume at 15°C; (2) relative density is the ratio of the mass of a given volume of liquid at 15°C to the mass of an equal volume of pure water at the same temperature; (3) specific gravity is the same as the relative density and the terms are used interchangeably.

Density (ASTM D-1298, IP 160) is an important property of petroleum products because petroleum and especially petroleum products are usually bought and sold on that basis or, if on a volume basis, then converted to mass basis via density measurements. This property is almost synonymously termed as density, relative density, gravity, and specific gravity, all terms related to each other. Usually a hydrometer, pycnometer, or more modern digital density meter is used for the determination of density or specific gravity (ASTM 2000; Speight, 2001).

In the most commonly used method (ASTM D-1298, IP 160), the sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle, and, after temperature equilibrium has been reached, the hydrometer scale is read and the temperature of the sample is noted.

Although there are many methods for the determination of density because of the different nature of petroleum itself and the different products, one test method (ASTM D-5002) is used for the determination of the density or relative density of petroleum that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C (59 and 95°F). This test method applies to petroleum products with high vapor pressures.
provided appropriate precautions are taken to prevent vapor loss during transfer of the sample to the density analyzer. In the method, approximately 0.7 ml of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in mass of the tube is used in conjunction with calibration data to determine the density of the sample.

Another test determines density and specific gravity by means of a digital densimeter (ASTM D-4052, IP 365). In the test, a small volume (approximately 0.7 ml) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample. The test is usually applied to petroleum, petroleum distillates, and petroleum products that are liquids at temperatures between 15 and 35°C (59 and 95°F) and have vapor pressures below 600 mmHg and viscosities below about 15,000 cSt at the temperature of the test. However, the method should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty.

Accurate determination of the density or specific gravity of crude oil is necessary for the conversion of measured volumes to volumes at the standard temperature of 15.56°C (60°F) (ASTM D-1250, IP 200, Petroleum Measurement Tables). The specific gravity is also a factor reflecting the quality of crude oils.

The accurate determination of the API gravity of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 60°F (15.56°C). Gravity is a factor governing the quality of crude oils. However, the gravity of a petroleum product is an uncertain indication of its quality. Correlated with other properties, gravity can be used to give approximate hydrocarbon composition and heat of combustion. This is usually accomplished though use of the API gravity, which is derived from the specific gravity:

\[ \text{API gravity (degrees)} = \left( \frac{141.5}{\text{sp gr 60/60°F}} \right) - 131.5 \]

and is also a critical measure for reflecting the quality of petroleum.

API gravity or density or relative density can be determined using one of two hydrometer methods (ASTM D-287, ASTM D-1298). The use of a digital analyzer (ASTM D-5002) is finding increasing popularity for the measurement of density and specific gravity.

In the method (ASTM D-287), the API gravity is determined using a glass hydrometer for petroleum and petroleum products that are normally handled as liquids and that have a Reid vapor pressure of 26 psi (180 kPa) or less. The API gravity is determined at 15.6°C (60°F), or converted
to values at 60°F, by means of standard tables. These tables are not applicable to non-hydrocarbons or essentially pure hydrocarbons such as the aromatics.

This test method is based on the principle that the gravity of a liquid varies directly with the depth of immersion of a body floating in it. The API gravity is determined with an hydrometer by observing the freely floating API hydrometer and noting the graduation nearest to the apparent intersection of the horizontal plane surface of the liquid with the vertical scale of the hydrometer after temperature equilibrium has been reached. The temperature of the sample is determined with a standard test thermometer that is immersed in the sample or with the thermometer that is an integral part of the hydrometer (thermohydrometer).

### 2.2.3. Distillation

The distillation tests give an indication of the types of products and the quality of the products that can be obtained from petroleum, and the tests are used to compare different petroleum types through the yield and quality of the 300°C (572°F) residuum fraction. For example, the waxiness or viscosity of this fraction gives an indication of the amount, types, and quality of the residual fuel that can be obtained from the petroleum. In this respect, the determination of the aniline point (ASTM D-611, IP 2) can be used to determine the aromatic or aliphatic character of petroleum. Although not necessarily the same as the wax content, correlative relationships can be derived from the data.

The basic method of distillation (ASTM D-86) is one of the oldest methods in use because the distillation characteristics of hydrocarbons have an important effect on safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of petroleum and derived products during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors. Several methods are available to define the distillation characteristics of petroleum and its various petroleum products. In addition to these physical methods, other test methods based on gas chromatography are also used to derive the boiling point distribution of a sample (ASTM D-2887, ASTM D-3710, ASTM D-5307, ASTM D-6352).

In the preliminary assay of petroleum the method of distillation is often used to give a rough indication of the boiling range of the crude (ASTM D-2892, IP 123). The test is carried out at atmospheric pressure and is stopped at 300°C (572°F) to avoid thermal decomposition. The distillate and the residuum can be further examined by tests such as specific gravity (ASTM D-1298, IP 160), sulfur content (ASTM D-129, IP 61), and viscos-
ity (ASTM D-445, IP 71). In fact, the use of a method (ASTM D-2569) developed for the determining the distillation characteristics of pitch allows further examination of residua.

In addition to the whole crude oil tests performed as part of the inspection assay, a comprehensive or full assay requires that the crude be fractionally distilled and the fractions characterized by the relevant tests. Fractionation of the crude oil begins with a true boiling point (TBP) distillation using a fractionating column with an efficiency of 14–18 theoretical plates and operated at a reflux ratio of 5:1 (ASTM D-2892). The TBP distillation may be used for all fractions up to a maximum cut point of about 350°C atmospheric equivalent temperature (AET), but a low residence time in the still (or reduced pressure) is needed to minimize cracking.

It is often useful to extend the boiling point data to higher temperatures than are possible in the fractionating distillation method previously described, and for this purpose a vacuum distillation in a simple still with no fractionating column (ASTM D-1160) can be carried out. This distillation, which is done under fractionating conditions equivalent to one theoretical plate, allows the boiling point data to be extended to about 600°C (1112°F) with many crude oils. This method gives useful comparative and reproducible results that are often accurate enough for refinery purposes, provided significant cracking does not occur.

Usually seven fractions provide the basis for a reasonably thorough evaluation of the distillation properties of the feedstock:

1. Gas, boiling range: <15.5°C (60°F)
2. Gasoline (light naphtha), boiling range: 15.5–149°C (60–300°F)
3. Kerosene (medium naphtha), boiling range: 149–232°C (300–450°F)
5. Light vacuum gas oil, boiling range: 343–371°C (650–700°F)
6. Heavy vacuum gas oil, boiling range: 371–566°C (700–1050°F)
7. Residuum, boiling range: >566°C (1050°F)

From 5 to 50 liters of crude oil are necessary to complete a full assay, depending on the number of fractions to be taken and the tests to be performed on the fractions.

A more recent test method (ASTM D-5236) is seeing increasing use and appears to be the method of choice for crude assay vacuum distillations. Wiped-wall or thin-film molecular stills can also be used to separate the higher-boiling fractions under conditions that minimize cracking. In these units, however, cut points cannot be directly selected because vapor temperature in the distillation column cannot be measured accurately under
operating conditions. Instead, the wall (film) temperature, pressure, and feed rate that will produce a fraction with a given end point are determined from in-house correlations developed by matching yields between the wiped-wall distillation and the conventional distillation (ASTM D-1160, ASTM D-5236). And wiped-wall stills are often used because they allow higher end points and can easily provide sufficient quantities of the fractions for characterization purposes.

2.2.4. Light Hydrocarbons

The amount of the individual light hydrocarbons in petroleum (methane to butane or pentane) is often included as part of the preliminary assay. Although one of the more conventional distillation procedures might be used, the determination of light hydrocarbons in petroleum is best is carried out with a gas chromatographic method (ASTM D-2427).

2.2.5. Metallic Constituents

Petroleum, as recovered from the reservoir, contains metallic constituents but also picks up metallic constituents during recovery, transportation, and storage. Even trace amounts of these metals can be deleterious to refining processes, especially processes in which catalysts are used. Trace components, such as metallic constituents, can also produce adverse effects in refining either (1) by causing corrosion or (2) by affecting the quality of refined products.

Hence, it is important to have test methods that can determine metals, both at trace levels and at major concentrations. Thus test methods have evolved that are used for the determination of specific metals as well as the multielement methods of determination using techniques such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, and X-ray fluorescence spectroscopy.

Nickel and vanadium along with iron and sodium (from the brine) are the major metallic constituents of crude oil. These metals can be determined by atomic absorption spectrophotometric methods (ASTM D-5863, IP 285, IP 288, IP 465), wavelength-dispersive X-ray fluorescence spectrometry (IP 433), and inductively coupled plasma emission spectrometry (ICPES). Several other analytical methods are available for the routine determination of trace elements in crude oil, some of which allow direct aspiration of the samples (diluted in a solvent) instead of time-consuming sample preparation procedures such as wet ashing (acid decomposition) or flame or dry ashing (removal of volatile/combustible constituents) (ASTM D-5863). Among the techniques used for trace element determinations are conductivity (IP 265), flameless and flame atomic absorption (AA) spectropho-
tometry (ASTM D-2788, ASTM D-5863), and inductively coupled argon plasma (ICP) spectrophotometry (ASTM D-5708).

Inductively coupled argon plasma emission spectrophotometry (ASTM D-5708) has an advantage over atomic absorption spectrophotometry (ASTM D-4628, ASTM D-5863) because it can provide more complete elemental composition data than the atomic absorption method. Flame emission spectroscopy is often used successfully in conjunction with atomic absorption spectrophotometry (ASTM D-3605). X-ray fluorescence spectrophotometry (ASTM D-4927, ASTM D-6443) is also sometimes used, but matrix effects can be a problem.

The method to be used for the determination of metallic constituents in petroleum is often a matter of individual preference.

### 2.2.6. Salt Content

The salt content of crude oil is highly variable and results principally from production practices used in the field and, to a lesser extent, from its handling aboard the tankers bringing it to terminals. The bulk of the salt present will be dissolved in coexisting water and can be removed in desalters, but small amounts of salt may be dissolved in the crude oil itself. Salt may be derived from reservoir or formation waters or from other waters used in secondary recovery operations. Aboard tankers, ballast water of varying salinity may also be a source of salt contamination.

Salt in crude oil may be deleterious in several ways. Even in small concentrations, salts will accumulate in stills, heaters, and exchangers, leading to fouling that requires expensive cleanup. More importantly, during flash vaporization of crude oil certain metallic salts can be hydrolyzed to hydrochloric acid according to the following reactions:

\[
2\text{NaCl} + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{Na}_2\text{O}
\]

\[
\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{MgO}
\]

The hydrochloric acid evolved is extremely corrosive, necessitating the injection of a basic compound, such as ammonia, into the overhead lines to minimize corrosion damage. Salts and evolved acids can also contaminate both overhead and residual products, and certain metallic salts can deactivate catalysts.

Thus knowledge of the content of salt in crude oil is important in deciding whether and to what extent the crude oil needs desalting.

The salt content is determined by potentiometric titration in a non-aqueous solution in which the conductivity of a solution of crude oil in a polar solvent is compared with that of a series of standard salt solutions in
the same solvent (ASTM D-3230). In this method, the sample is dissolved in a mixed solvent and placed in a test cell consisting of a beaker and two parallel stainless steel plates. An alternating voltage is passed through the plates, and the salt content is obtained by reference to a calibration curve of the relationship of salt content of known mixtures to the current.

It is necessary, however, to use other methods, such as atomic absorption, inductively coupled argon plasma emission spectrophotometry, and ion chromatography to determine the composition of the salts present. A method involving application of extraction and volumetric titration is also used (IP 77).

2.2.7. Sulfur Content

Sulfur is present in petroleum as sulfides, thiophenes, benzothiophenes, and dibenzothiophenes. In most cases, the presence of sulfur is detrimental to the processing because sulfur can act as catalytic poisons during processing.

The sulfur content of petroleum is an important property and varies widely within the rough limits 0.1% w/w to 3.0% w/w, and a sulfur content up to 8.0% w/w has been noted for tar sand bitumen. Compounds containing this element are among the most undesirable constituents of petroleum because they can give rise to plant corrosion and atmospheric pollution. Petroleum can evolve hydrogen sulfide during distillation as well as low-boiling sulfur compounds.

Hydrogen sulfide may be evolved during the distillation process either from free hydrogen sulfide in the feedstocks or because of low-temperature thermal decomposition of sulfur compounds; the latter is less likely than the former. Generally, however, the sulfur compounds concentrate in the distillation residue (Speight, 2000), the volatile sulfur compounds in the distillates being removed by such processes as hydrofining and caustic washing (Speight, 1999). The sulfur content of fuels obtained from petroleum residua and the atmospheric pollution arising from the use of these fuels is an important factor in petroleum utilization, so that the increasing insistence on a low-sulfur-content fuel oil has increased the value of low-sulfur petroleum.

Sulfur compounds contribute to corrosion of refinery equipment and poisoning of catalysts, cause corrosiveness in refined products, and contribute to environmental pollution as a result of the combustion of fuel products. Sulfur compounds may be present throughout the boiling range of crude oils although, as a rule, they are more abundant in the higher-boiling fractions. In some crude oils, thermally labile sulfur compounds can decompose on heating to produce hydrogen sulfide, which is corrosive and toxic.

A considerable number of tests are available to estimate the sulfur in petroleum or to study its effect on various products. Hydrogen sulfide dis-
solved in petroleum is normally determined by absorption of the hydrogen sulfide in a suitable solution that is subsequently analyzed chemically (Doctor method) (ASTM, D-4952, IP 30) or by the formation of cadmium sulfate (IP 103).

The Doctor test measures the amount of sulfur available to react with metallic surfaces at the temperature of the test. The rates of reaction are metal type-, temperature-, and time dependent. In the test, a sample is treated with copper powder at 149°C or 300°F. The copper powder is filtered from the mixture. Active sulfur is calculated from the difference between the sulfur contents of the sample (ASTM D-129) before and after treatment with copper.

Sulfur that is chemically combined as an organic constituent of crude is usually estimated by oxidizing a sample in a bomb and converting the sulfur compounds to barium sulfate that is determined gravimetrically (ASTM D-129, IP 61). This method is applicable to any sample of sufficiently low volatility (e.g., a residuum or tar sand bitumen) that can be weighed accurately in an open sample boat and that contains at least 0.1% sulfur. In this method, the sample is oxidized by combustion in a pressure vessel (bomb) containing oxygen under pressure. The sulfur in the sample is converted to sulfate and from the bomb washings is gravimetrically determined as barium sulfate. However, the method is not applicable to samples containing elements that give residues, other than barium sulfate, that are insoluble in dilute hydrochloric acid and would interfere in the precipitation step. In addition, the method is also subject to inaccuracies that arise from interference by the sediment inherently present in petroleum.

Until recently, one of the most widely used methods for determination of total sulfur content has been combustion of a sample in oxygen to convert the sulfur to sulfur dioxide, which is collected and subsequently titrated iodometrically or detected by nondispersive infrared (ASTM D-1552). This method is particularly applicable to heavier oil and fractions such as residua that boil above 177°C (350°F) and contain more than 0.06% w/w sulfur. In addition, the sulfur content of petroleum coke containing up to 8% w/w sulfur can be determined.

In the iodate detection system, the sample is burned in a stream of oxygen at a sufficiently high temperature to convert the sulfur to sulfur dioxide. The combustion products are passed into an absorber that contains an acidic solution of potassium iodide and starch indicator. A faint blue color is developed in the absorber solution by the addition of standard potassium iodate solution and as combustion proceeds, bleaching the blue color, more iodate is added. From the amount of standard iodate consumed during the combustion, the sulfur content of the sample is calculated.

In the infrared detection system, the sample is weighed into a special ceramic boat that is then placed into a combustion furnace at 1371°C
(2500°F) in an oxygen atmosphere. Moisture and dust are removed with traps, and the sulfur dioxide is measured with an infrared detector.

The lamp combustion method (ASTM D-1266, IP 107) and the Wickbold combustion method (IP 243) are used for the determination of sulfur in petroleum and as trace quantities of total sulfur in petroleum products and are related to various other methods (ASTM D-2384, ASTM D-2784, ASTM D-2785, ASTM D-4045)

In the lamp method (ASTM D-1266, IP 107), a sample is burned in a closed system using a suitable lamp and an artificial atmosphere composed of 70% carbon dioxide and 30% oxygen to prevent formation of nitrogen oxides. The sulfur oxides are absorbed and oxidized to sulfuric acid ($\text{H}_2\text{SO}_4$) by means of hydrogen peroxide ($\text{H}_2\text{O}_2$) solution that is then flushed with air to remove dissolved carbon dioxide. Sulfur as sulfate in the absorbent is determined acidimetrically by titration with standard sodium hydroxide ($\text{NaOH}$) solution. Alternatively, the sample can be burned in air and the sulfur as sulfate in the absorbent determined gravimetrically as barium sulfate ($\text{BaSO}_4$) after precipitation. If the sulfur content of the sample is less than 0.01% w/w, it is necessary to determine sulfur in the absorber solution turbidimetrically as barium sulfate.

The older, classic techniques for sulfur determination are being supplanted by two instrumental methods (ASTM D-2622, ASTM D-4294, IP 447).

In the first method (ASTM D-2622), the sample is placed in an X-ray beam, and the peak intensity of the sulfur $K\alpha$ line at 5.373 Å is measured. The background intensity, measured at 5.190 Å, is subtracted from the peak intensity, and the resultant net counting rate is then compared with a previously prepared calibration curve or equation to obtain the sulfur concentration in % w/w.

The second method (ASTM D-4294, IP 477) uses energy-dispersive X-ray fluorescence spectroscopy, has slightly better repeatability and reproducibility than the high-temperature method, and is adaptable to field applications but can be affected by some commonly present interferences such as halides. In this method, the sample is placed in a beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standard to obtain the sulfur concentration. Two groups of calibration standards are required to span the concentration range, one standard ranges from 0.015% to 0.1% w/w sulfur and the other from 0.1% to 5.0% w/w sulfur.

### 2.2.8. Viscosity and Pour Point

Viscosity and pour point determinations are performed principally to ascertain the handling (flow) characteristics of petroleum at low temperatures.
There are, however, some general relationships of crude oil composition that can be derived from pour point and viscosity data. Commonly, the lower the pour point of a crude oil the more aromatic it is, and the higher the pour point the more paraffinic it is.

Viscosity is usually determined at different temperatures (e.g., 25°C/77°F, and 100°C/212°F) by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer (ASTM D-445).

In the test, the time for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature is measured in seconds. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. Conversion of the kinematic viscosity in centistokes (cSt) at any temperature to Saybolt Universal viscosity in Saybolt Universal seconds (SUS) at the same temperature and for converting kinematic viscosity in centistokes at 122 and 210°F to Saybolt Furol viscosity in Saybolt Furol seconds (SFS) at the same temperatures (ASTM D-2161) is available through formulae.

The viscosity index (ASTM D-2270, IP 226) is a widely used measure of the variation in kinematic viscosity due to changes in the temperature of petroleum between 40°C and 100°C (104°F and 212°F). For crude oils of similar kinematic viscosity, the higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The accuracy of the calculated viscosity index is dependent only on the accuracy of the original viscosity determination.

The pour point of petroleum is an index of the lowest temperature at which the crude oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where petroleum, depending on its thermal history, might appear in the liquid as well as the solid state. The pour point data can be used to supplement other measurements of cold flow behavior, and the data are particularly useful for the screening of the effect of wax interaction modifiers on the flow behavior of petroleum.

In the original (and still widely used) test for pour point (ASTM D-97, IP 15), a sample is cooled at a specified rate and examined at intervals of 3°C (5.4°F) for flow characteristics. The lowest temperature at which the movement of the oil is observed is recorded as the pour point.

A later test method (ASTM D-5853) covers two procedures for the determination of the pour point of crude oils down to –36°C. One method provides a measure of the maximum (upper) pour point temperature. The second method measures the minimum (lower) pour point temperature. In these methods, the test specimen is cooled (after preliminary heating) at a specified rate and examined at intervals of 3°C (5.4°F) for flow character-
istics. Again, the lowest temperature at which movement of the test specimen is observed is recorded as the pour point.

In any determination of the pour point, petroleum that contains wax produces an irregular flow behavior when the wax begins to separate. Such petroleum possesses viscosity relationships that are difficult to predict in pipeline operation. In addition, some waxy petroleum is sensitive to heat treatment that can also affect the viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy petroleum. However, laboratory pumpability tests (ASTM D-3245, IP 230) are available that give an estimate of minimum handling temperature and minimum line or storage temperature.

2.2.9. Water and Sediment

Considerable importance is attached to the presence of water or sediment in petroleum because they lead to difficulties in the refinery, for example, corrosion of equipment, uneven running on the distillation unit, blockages in heat exchangers, and adverse effects on product quality.

The water and sediment content of crude oil, like salt, results from production and transportation practices. Water, with its dissolved salts, may occur as easily removable suspended droplets or as an emulsion. The sediment dispersed in crude oil may be comprised of inorganic minerals from the production horizon or from drilling fluids and scale and rust from pipelines and tanks used for oil transportation and storage. Usually water is present in far greater amounts than sediment, but, collectively, it is unusual for them to exceed 1% of the crude oil on a delivered basis. Like salt, water and sediment can foul heaters, stills, and exchangers and can contribute to corrosion and to deleterious product quality. Also, water and sediment are principal components of the sludge that accumulates in storage tanks and must be disposed of periodically in an environmentally acceptable manner. Knowledge of the water and sediment content is also important in accurately determining net volumes of crude oil in sales, taxation, exchanges, and custody transfers.

The sediment consists of finely divided solids that may be drilling mud or sand or scale picked up during the transport of the oil or may consist of chlorides derived from evaporation of brine droplets in the oil. The solids may be dispersed in the oil or carried in water droplets. Sediment in petroleum can lead to serious plugging of equipment, corrosion due to chloride decomposition, and a lowering of residual fuel quality.

Water may be found in the crude either in an emulsified form or in large droplets and can cause flooding of distillation units and excessive accumulation of sludge in tanks. Refiners generally limit the quantity, and although steps are normally taken at the oil field to reduce the water content as much
as possible, water may be introduced later during shipment. In any form, water and sediment are highly undesirable in a refinery feedstock, and the relevant tests involving distillation (ASTM D-95, ASTM D-4006, IP 74, IP 358), centrifuging (ASTM D-96, ASTM D-4007), extraction (ASTM D-473, IP 53), and the Karl Fischer titration (ASTM D-4377, ASTM D-4928, IP 356, IP 386, IP 438, IP 439) are regarded as important in petroleum quality examinations.

Before the assay it is sometimes necessary to separate the water from a petroleum sample. Certain types of petroleum, notably heavy oil, often form persistent emulsions that are difficult to separate. On the other hand, in testing wax-bearing petroleum for sediment and water care must be taken to ensure that wax suspended in the sample is brought into solution before the test; otherwise it will be recorded as sediment.

The Karl Fischer test method (ASTM D-1364, ASTM D-6304) covers the direct determination of water in petroleum. In the test, the sample injection in the titration vessel can be performed on a volumetric or gravimetric basis. Viscous samples can be analyzed with a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry, inert carrier gas.

Water and sediment in petroleum can be determined simultaneously (ASTM D-96, ASTM D-4007, IP 359) by the centrifuge method. Known volumes of petroleum and solvent are placed in a centrifuge tube and heated to 60°C (140°F). After centrifugation, the volume of the sediment-and-water layer at the bottom of the tube is read. For petroleum that contains wax, a temperature of 71°C (160°F) or higher may be required to completely melt the wax crystals so that they are not measured as sediment.

Sediment is also determined by an extraction method (ASTM D-473, IP 53) or by membrane filtration (ASTM D-4807). In the former method (ASTM D-473, IP 53), an oil sample contained in a refractory thimble is extracted with hot toluene until the residue reaches a constant mass. In the latter test, the sample is dissolved in hot toluene and filtered under vacuum through a 0.45-µm-porosity membrane filter. The filter with residue is washed, dried, and weighed.

### 2.2.10. Wax Content

Petroleum with a high wax content presents difficulties in handling and pumping as well as producing distillate and residual fuels of high pour point and lubricating oils that are costly to dewax.

All the standard methods for the determination of wax involve precipitating the wax from solvents such as methylene chloride or acetone under specified conditions of solvent-to-oil ratio and temperature. Measurements such as these give comparative results that are often useful in characteriz-
ing the wax content of petroleum or for investigating factors involved in flow problems.

On the other hand, the wax appearance point (ASTM D-3117) may be determined by cooling of a sample under prescribed conditions with stirring. The temperature at which the wax first appears is the wax appearance point.

2.2.11. Other Tests

The inspection assay tests discussed above are not exhaustive but are the ones most commonly used and provide data on the impurities present as well as a general idea of the products that may be recoverable. Other properties that are determined on an as-needed basis include, but are not limited to, the following: (1) vapor pressure (Reid method) (ASTM D-323, IP 69, IP 402), (2) total acid number (ASTM D-664, IP 177), and chloride content (ASTM D-4929, IP 244).

The Reid vapor pressure test method (ASTM D-323, IP 69) measures the vapor pressure of volatile petroleum. The Reid vapor pressure differs from the true vapor pressure of the sample because of some small sample vaporization and the presence of water vapor and air in the confined space.

The acid number is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in this solvent to a green/green-brown end point, using p-naphtholbenzein indicator solution. The strong acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared nonaqueous acidic buffer solution or a well-defined inflection point as specified in the test method (ASTM D-664, IP 177).

To determine the acid number by the color indicator method (ASTM D-974, IP 139), the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end point indicated by the color change of the added p-naphtholbenzein solution (orange in acid and green-brown in base). To determine the strong acid number, a separate portion of the sample is extracted with hot water and the aqueous extract is titrated with potassium hydroxide solution, using methyl orange as an indicator.

To determine the acid number by the potentiometric titration method (ASTM D-664, IP 177), the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a calomel reference electrode. The meter readings are plotted
manually or automatically against the respective volumes of titrating solution, and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those found for freshly prepared nonaqueous acidic and basic buffer solutions.

The acid numbers obtained by this color indicator test method (ASTM D-974, IP 139) may or may not be numerically the same as those obtained by the potentiometric titration method (ASTM D-664, IP 177). In addition, the color of the crude oil sample can interfere with observation of the end point when the color indicator method is used. Determination of the acid number is more appropriate for various petroleum products.

The test method for the determination of the acid number by the color indicator titration method (ASTM D-3339, IP 431) measures the acid number of oils obtained from a laboratory oxidation test (ASTM D-943) using smaller amounts of samples than those used in other acid number tests (ASTM D-664, ASTM D-974, IP 139, IP 177).

In this test, the sample is dissolved in a solvent mixture of toluene, isopropyl alcohol, and a small amount of water and the solution is titrated at room temperature under a nitrogen atmosphere with standard potassium hydroxide (KOH) in isopropyl alcohol to the stable green color of the added indicator \( p \)-naphtholbenzein. Dark-colored crude oils (and crude oil products) are more difficult to analyze by this method because of the difficulty in detecting color change. In such cases, the potentiometric titration method (ASTM D-664, IP 177) may be used if sufficient sample is available.

The acid numbers will not provide the data essential to determining whether a specific petroleum or a blend with other crude oils will yield the desired product slate. Such data can only be generated when a comprehensive petroleum assay is performed and the data from several tests are taken in relation to each other.

The aniline point (or mixed aniline point) (ASTM D-611, IP 2) has been used for the characterization of crude oil, although it is more applicable to pure hydrocarbons and in their mixtures and is used to estimate the aromatic content of mixtures. Aromatics exhibit the lowest aniline points and paraffins the highest aniline points. Cycloparaffins and olefins exhibit values between these two extremes. In any hydrocarbon homologous series the aniline point increases with increasing molecular weight.

With the data derived from the test assay, it is possible to assess petroleum quality to acquire a degree of predictability of performance during refining. However, a knowledge of the basic concepts of refining will help the analyst understand the production and, to a large extent, the anticipated properties of the product, which in turn are related to storage, sampling, and handling of the products.
2.3. PETROLEUM REFINING

Petroleum is rarely used in its raw form but must instead be processed into its various products, generally as a means of forming products with a hydrogen content different from that of the original feedstock. Thus the chemistry of the refining process is concerned primarily with the production not only of better products but also of salable materials.

Petroleum contains many thousands of different compounds that vary in molecular weight from 16 (methane, CH\(_4\)) to more than 2000 (Speight, 1999, 2001 and references cited therein). This broad range in molecular weights results in boiling points that range from \(-160^\circ\text{C} (-288^\circ\text{F})\) to temperatures in excess of \(1100^\circ\text{C} (2000^\circ\text{F})\) (Speight, 2001).

In brief, a refinery must be recognized as a complex network of integrated unit processes for the purpose of producing a variety of products from petroleum (Fig. 2.2) (Speight, 1999; Speight and Ozum, 2002). Each refinery has its own range of preferred petroleum feedstock from which a desired distribution of products is obtained. Nevertheless, refinery processes can be divided into three major types:

1. **Separation**: division of petroleum into various streams (or fractions) depending on the nature of the crude material.
2. **Conversion**: production of salable materials from petroleum, usually by skeletal alteration, or even by alteration of the chemical type, of the petroleum constituents.
3. **Finishing**: purification of various product streams by a variety of processes that essentially remove impurities from the product; for convenience, processes that accomplish molecular alteration, such as reforming, are also included in this category.

The separation and finishing processes may involve distillation or even treatment with a wash solution, either to remove impurities or, in the case of distillation, to produce a material boiling over a narrower range, and the chemistry of these processes is quite simple.

Conversion processes are, in essence, processes that change the number of carbon atoms per molecule, alter the molecular hydrogen-to-carbon ratio, or change the molecular structure of the material without affecting the number of carbon atoms per molecule (Fig. 2.2). These latter processes (isomerization processes) essentially change the shape of the molecule(s) and are used to improve the quality of the product (Speight, 1999; Speight and Ozum, 2002).

Thermal cracking processes are commonly used to convert petroleum residua into distillable liquid products; examples of thermal cracking processes currently in use are visbreaking and coking (delayed coking,
fluid coking, and flexicoking). In all of these processes the simultaneous formation of sediment or coke limits the conversion to usable liquid products (Speight, 1999; Speight and Ozum 2002 and references cited therein).
2.3.1. Visbreaking

The visbreaking process is used primarily a means of reducing the viscosity of heavy feedstocks by *controlled thermal decomposition* insofar as the hot products are quenched before complete conversion can occur (Speight, 1999). However, the process is often plagued by sediment formation in the products. This sediment, or sludge, must be removed if the products are to meet fuel oil specifications.

The process (Fig. 2.3) uses the mild thermal cracking (*partial conversion*) as a relatively low-cost and low-severity approach to improving the viscosity characteristics of the residue without attempting significant conversion to distillates. Low residence times are required to avoid polymerization and coking reactions, although additives can help to suppress coke deposits on the tubes of the furnace.

A visbreaking unit consists of a reaction furnace, followed by quenching with a recycled oil, and fractionation of the product mixture. All of the reaction in this process occurs as the oil flows through the tubes of the reaction furnace. The severity is controlled by the flow rate through the furnace and the temperature; typical conditions are 475–500°C (885–930°F) at the furnace exit with a residence time of 1–3 minutes; operation for 3–6 months on stream (continuous use) is possible before the furnace tubes must be

![Figure 2.3. The visbreaking process](image-url)
cleaned and the coke removed. The operating pressure in the furnace tubes can range from 0.7 to 5 MPa depending on the degree of vaporization and the residence time desired. For a given furnace tube volume, a lower operating pressure will reduce the actual residence time of the liquid phase.

### 2.3.2. Coking

*Coking,* as the term is used in the petroleum industry, is a process for converting nondistillable fractions (residua) of petroleum to lower-boiling products and coke. Coking is often used in preference to catalytic cracking because of the presence of metals and nitrogen components that poison catalysts (Speight and Ozum, 2002).

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

*Delayed coking* (Fig. 2.4) is the oldest, most widely used process and has changed very little in the five or more decades in which it has been on stream in refineries.

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

**Figure 2.4.** The delayed coking process
continuous processing. The process can be operated on a cycle, typically 24–48 hours.

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

*Fluid coking* (Fig. 2.5) is a continuous fluidized solids process that cracks feed thermally over heated coke particles in a reactor vessel to gas, liquid products, and coke. Heat for the process is supplied by partial combustion of the coke, with the remaining coke being drawn as product. The new coke is deposited in a thin, fresh layer on the outside surface of the circulating coke particle.

Small particles of coke made in the process circulate in a fluidized state between the vessels and are the heat transfer medium. Thus the process requires no high-temperature preheat furnace. Fluid coking is carried out at essentially atmospheric pressure and temperatures in excess of 485°C (900°F) with residence times on the order of 15–30 seconds. The longer residence time is in direct contrast to the delayed coking process, in which the coking reactions are allowed to proceed to completion. This is evident

![Figure 2.5. The fluid coking process](image)
from the somewhat higher liquid yields observed in many fluid coking processes. However, the products from a fluid coker may be somewhat more olefinic and slightly less desirable for downstream processing. The *flexicoking* process is a modification of the fluid coking process that includes a gasifier adjoining the burner/regenerator to convert excess coke to a clean fuel gas with a heating value of about 90 Btu/ft³. The coke gasification can be controlled to burn about 95% of the coke to maximize production of coke gas or to operate at a reduced level to produce both gas and a coke. This flexibility permits adjustment for coke market conditions over a considerable range of feedstock properties.

The *liquid products* from the coker can, after cleanup via commercially available hydrodesulfurization technology (Speight, 2001), provide low-sulfur liquid fuels (less than 0.2% w/w sulfur). Coker naphtha has a boiling range up to 220°C (430°F), are olefinic, and must be upgraded by hydrogen processing for removal of olefins, sulfur, and nitrogen. They are then used conventionally for reforming to gasoline or chemicals feedstock. Middle distillates, boiling in the range of 220–360°C (430–680°F), are also hydrogen treated for improved storage stability, sulfur removal, and nitrogen reduction. They can then be used as precursors to gasoline, diesel fuel, or fuel oil. The gas oil boiling up to 510°C (950°F) is usually low in metals and may be used as the feedstock for fluid catalytic cracking.

Another major application for the coking processes is in upgrading heavy (high viscosity), low-value petroleum into lighter products.

Petroleum *coke* is used principally as a fuel or, after calcining, for carbon electrodes. The feedstock from which the coke is produced controls the coke properties, especially sulfur, nitrogen, and metal content. A concentration effect tends to deposit the majority of the sulfur, nitrogen, and metals in the coke. Cokes exceeding about 2.5% sulfur content and 200 ppm vanadium are mainly used, environmental regulations permitting, for fuel or fuel additives. The properties of coke for non-fuel use include a low sulfur, metal, and ash content as well as a definable physical structure.

### 2.3.3. Hydroprocessing

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

*Hydrotreating* is defined as the lower-temperature removal of heteroatomic species by treatment of a feedstock or product in the presence of hydrogen. On the other hand, *hydrocracking* (Fig. 2.6) is the thermal decomposition (in the presence of hydrogen) of a feedstock in which carbon-carbon bonds are cleaved in addition to the removal of hetero-
atomic species (nitrogen, oxygen, and sulfur) as the respective hydrogenated analogs (ammonia, NH₃, water, H₂O, and hydrogen sulfide, H₂S). In reality, hydrotreating and hydrocracking may occur simultaneously.

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

2.4. NATURAL GAS

2.4.1. Definition

Natural gas is the gaseous mixture associated with petroleum reservoirs and is predominantly methane but does contain other combustible hydrocarbon compounds as well as non-hydrocarbon compounds (Table 2.3; Speight, 1999). In fact, associated natural gas is believed to be the most economical form of ethane.

The gas occurs in the porous rock of the earth’s crust either alone or with accumulations of petroleum. In the latter case, the gas forms the gas cap, which is the mass of gas trapped between the liquid petroleum and the impervious cap rock of the petroleum reservoir. When the pressure in the reservoir is sufficiently high, the natural gas may be dissolved in the petroleum and released on penetration of the reservoir as a result of drilling operations.

![Figure 2.6. The hydrocracking process](image-url)
The principal types of gaseous fuels are oil (distillation) gas, reformed natural gas, and reformed propane or liquefied petroleum gas (LPG). **Mixed gas** is a gas prepared by adding natural gas or LPG to a manufactured gas, giving a product of better utility and higher heat content or Btu value.

**Liquefied petroleum gas** (LPG) is the term applied to certain specific hydrocarbons and their mixtures, which exist in the gaseous state under atmospheric ambient conditions but can be converted to the liquid state under conditions of moderate pressure at ambient temperature. Thus LPG is a hydrocarbon mixture containing propane (CH₃CH₂CH₃), butane (CH₃CH₂CH₂CH₃), iso-butane [CH₃CH((CH₃)CH₃] and to a lesser extent propylene (CH₃CH:CH₂), or butylene (CH₃CH₂CH:CH₂). The most common commercial products are propane, butane, or some mixture of the two and are generally extracted from natural gas or crude petroleum. Propylene and butylenes result from the cracking of other hydrocarbons in a petroleum refinery and are two important chemical feedstocks.

### 2.4.2. Composition

The principal constituent of natural gas is methane (CH₄). Other constituents are paraffinic hydrocarbons such as ethane (CH₃CH₃), propane, and the butanes. Many natural gases contain nitrogen (N₂) as well as carbon dioxide (CO₂) and hydrogen sulfide (H₂S). Trace quantities of argon, hydro-

<table>
<thead>
<tr>
<th>Category</th>
<th>Component</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic</td>
<td>Methane (CH₄)</td>
<td>70–98</td>
</tr>
<tr>
<td></td>
<td>Ethane (C₂H₆)</td>
<td>1–10</td>
</tr>
<tr>
<td></td>
<td>Propane (C₃H₈)</td>
<td>Trace–5</td>
</tr>
<tr>
<td></td>
<td>Butane (C₄H₁₀)</td>
<td>Trace–2</td>
</tr>
<tr>
<td></td>
<td>Pentane (C₅H₁₂)</td>
<td>Trace–1</td>
</tr>
<tr>
<td></td>
<td>Hexane (C₆H₁₄)</td>
<td>Trace–0.5</td>
</tr>
<tr>
<td></td>
<td>Heptane and higher (C₇⁺)</td>
<td>None–trace</td>
</tr>
<tr>
<td>Cyclic</td>
<td>Cyclopropane (C₃H₆)</td>
<td>Traces</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane (C₆H₁₂)</td>
<td>Traces</td>
</tr>
<tr>
<td>Aromatic</td>
<td>Benzene (C₆H₆), others</td>
<td>Traces</td>
</tr>
<tr>
<td>Non-hydrocarbon</td>
<td>Nitrogen (N₂)</td>
<td>Trace–15</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide (CO₂)</td>
<td>Trace–1</td>
</tr>
<tr>
<td></td>
<td>Hydrogen sulfide (H₂S)</td>
<td>Trace occasionally</td>
</tr>
<tr>
<td></td>
<td>Helium (He)</td>
<td>Trace–5</td>
</tr>
<tr>
<td></td>
<td>Other sulfur and nitrogen compounds</td>
<td>Trace occasionally</td>
</tr>
<tr>
<td></td>
<td>Water (H₂O)</td>
<td>Trace–5</td>
</tr>
</tbody>
</table>

[Table 2.3. Composition of Associated Natural Gas From a Petroleum Well (adapted from Speight, 1999)]
gen, and helium may also be present. Generally, the hydrocarbons having a higher molecular weight than methane, carbon dioxide, and hydrogen sulfide are removed from natural gas before its use as a fuel. Gases produced in a refinery contain methane, ethane, ethylene, propylene, hydrogen, carbon monoxide, carbon dioxide, and nitrogen, with low concentrations of water vapor, oxygen, and other gases.

Types of natural gas vary according to composition. There is dry gas or lean gas, which is mostly methane, and wet gas, which contains considerable amounts of higher-molecular-weight and higher-boiling hydrocarbons (Table 2.4). Sour gas contains high proportions of hydrogen sulfide, whereas sweet gas contains little or no hydrogen sulfide. Residue gas is the gas remaining (mostly methane) after the higher-molecular-weight paraffins have been extracted. Casinghead gas is the gas derived from an oil well by extraction at the surface. Natural gas has no distinct odor and its main use is for fuel, but it can also be used to make chemicals and liquefied petroleum gas.

Some natural gas wells also produce helium, which can occur in commercial quantities; nitrogen and carbon dioxide are also found in some natural gases. Gas is usually separated at as high a pressure as possible, reducing compression costs when the gas is to be used for gas lift or de-

Table 2.4. General Composition of Wet and Dry Natural Gas (adapted from Speight, 1999)

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Wet</th>
<th>Range</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>84.6</td>
<td>96.0</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>6.4</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>5.3</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Isobutane</td>
<td>1.2</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>1.4</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Isopentane</td>
<td>0.4</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.2</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Hexanes</td>
<td>0.4</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Heptanes</td>
<td>0.1</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Non-hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td></td>
<td>0–5</td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td></td>
<td>0–0.5</td>
<td></td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td></td>
<td>0–5</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td>0–10</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td></td>
<td>0–0.05</td>
<td></td>
</tr>
<tr>
<td>Radon, krypton, xenon</td>
<td></td>
<td>Traces</td>
<td></td>
</tr>
</tbody>
</table>
livered to a pipeline. After gas removal, lighter hydrocarbons and hydrogen sulfide are removed as necessary to obtain a petroleum of suitable vapor pressure for transport yet retaining most of the natural gasoline constituents.

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

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

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

As with petroleum, natural gas from different wells varies widely in composition and analyses (Speight, 1990 and references cited therein; Speight, 1993 and references cited therein; Speight, 1999), and the proportion of non-hydrocarbon constituents can vary over a very wide range. Thus a particular natural gas field could require production, processing, and handling protocols different from those used for gas from another field.

The non-hydrocarbon constituents of natural gas can be classified as two types of materials: (1) diluents, such as nitrogen, carbon dioxide, and water vapors, and (2) contaminants, such as hydrogen sulfide and/or other sulfur compounds.

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

1. Acid gas, which is predominantly hydrogen sulfide, although carbon dioxide does occur to a lesser extent;
2. Water, which includes all entrained free water or water in condensed forms;
3. Liquids in the gas, such as higher-boiling hydrocarbons as well as pump lubricating oil, scrubber oil, and, on occasion, methanol; and
4. Any solid matter that may be present, such as fine silica (sand) and scaling from the pipe.

2.4.3. Properties and Test Methods

The composition of natural and process gases can vary so widely that no single set of specifications can possibly cover all of the tests necessary to define the specifications. The requirements are usually based on performances in burners and equipment, on minimum heat content, and on maximum sulfur content.

Because natural gas as delivered to pipelines has practically no odor, the addition of an odorant is required by most regulations so that the presence of the gas can be detected readily in case of accidents and leaks. This odorization is provided by the addition of trace amounts of some organic sulfur compounds to the gas before it reaches the consumer. The standard requirement is that a user will be able to detect the presence of the gas by odor when the concentration reaches 1% of gas in air. Because the lower limit of flammability of natural gas is approximately 5%, this 1% requirement is essentially equivalent to one-fifth the lower limit of flammability. The combustion of these trace amounts of odorant does not create any serious problems of sulfur content or toxicity.

The different methods for measuring gas composition include absorption, distillation, combustion, mass spectroscopy, infrared spectroscopy, and gas chromatography (ASTM D-2163, ASTM D-2650, and ASTM D-4424). Absorption methods involve absorbing individual constituents one at a time in suitable solvents and recording of contraction in volume measured. Distillation methods depend on the separation of constituents by fractional distillation and measurement of the volumes distilled. In combustion methods, certain combustible elements are caused to burn to carbon dioxide and water and the volume changes are used to calculate composition. Infrared spectroscopy is useful in particular applications. For the most accurate analyses, mass spectroscopy and gas chromatography are the preferred methods.

The specific gravity of product gases, including LPG, may be determined conveniently by a number of methods and a variety of instruments (ASTM D-1070, ASTM D-4891).
The heat value of gases is generally determined at constant pressure in a flow calorimeter in which the heat released by the combustion of a definite quantity of gas is absorbed by a measured quantity of water or air. A continuous recording calorimeter is available for measuring heat values of natural gases (ASTM D-1826).

The lower and upper limits of flammability indicate the percentage of combustible gas in air below which and above which flame will not propagate. When flame is initiated in mixtures having compositions within these limits it will propagate, and therefore the mixtures are flammable. A knowledge of flammable limits and their use in establishing safe practices in handling gaseous fuels is important, for example, when purging equipment used in gas service, in controlling factory or mine atmospheres, or in handling liquefied gases.

Many factors enter into the experimental determination of flammable limits of gas mixtures, including the diameter and length of the tube or vessel used for the test, the temperature and pressure of the gases, and the direction of flame propagation—upward or downward. For these and other reasons, great care must be used in the application of the data. In monitoring closed spaces where small amounts of gases enter the atmosphere, often the maximum concentration of the combustible gas is limited to one-fifth of the concentration of the gas at the lower limit of flammability of the gas-air mixture.

2.5. NATURAL GAS LIQUIDS AND NATURAL GASOLINE

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

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

Chemical manufacturers use ethane in making ethylene, an important petrochemical. Butane and propane, and mixtures of the two, are classified as liquefied petroleum gas (LPG), which is used chiefly as a heating fuel in industry and in homes. Pentane, hexane, and heptane are called natural gasoline or condensate and are used for blending with refinery gasoline.

The extraction of natural gas liquids from natural gas is achieved by the application of refining techniques that result in fractionation of the natural gas into its hydrocarbon constituents. There are two main methods of producing natural gas liquids: (1) condensation and (2) absorption. In condensation, natural gas is chilled until it becomes a liquid from which the natural
gas liquids are extracted. In absorption, processors mix gas with an oil that absorbs light hydrocarbons and the natural gas liquids are distilled from the oil.

Another product is gas condensate, which contains relatively high amounts of the higher-molecular-weight liquid hydrocarbons. These hydrocarbons may occur in the gas phase in the reservoir.

Normally the gas in a gas cap contains methane and other hydrocarbons that may be separated out by compressing the gas. A well-known example is natural gasoline, which was formerly referred to as casinghead gasoline or natural gas gasoline. However, at high pressures such as those existing in the deeper fields, the density of the gas increases and the density of the oil decreases until they form a single phase in the reservoir.

Wet natural gas contains natural gasoline in vapor form. The wet gas, also known as casinghead gas, is chiefly a mixture of methane, ethane, and the volatile hydrocarbons propane, butane, pentane \( (C_5H_{12}) \), hexane \( (C_6H_{14}) \), and heptane \( (C_7H_{16}) \). The latter three hydrocarbons form the main constituents of natural gasoline, which is recovered in refineries in liquid form mainly by absorption or compression processes. Pentane, hexane, and heptane are liquids under normal atmospheric conditions and are the chief components of ordinary refinery gasoline.

Natural gasoline is used as blending stock for refinery gasoline and may be cracked to produce lower-boiling products, such as ethylene, propylene, and butylene. Caution should be taken not to confuse natural gasoline with straight-run gasoline (often also incorrectly referred to as natural gasoline), which is the gasoline distilled unchanged from petroleum.

The various tests that are applied to specifications for this group of low-boiling liquids will be referenced in the chapters dealing with liquefied petroleum gas (Chapter 3), naphtha (Chapter 4), and gasoline (Chapter 5).

2.6. PETROLEUM CHARACTER AND BEHAVIOR

The data derived from any one or more of the analytical techniques give an indication of the characteristics of petroleum and an indication of the methods of feedstock processing as well as for the predictability of product yields and properties (Dolbear et al., 1987; Adler and Hall, 1988; Wallace and Carrigy, 1988; Al-Besharah et al., 1989; Speight, 1999, 2000, 2001 and references cited therein).

The most promising means of predictability of feedstock behavior during processing and predictability of product yields and properties has arisen from the concept of feedstock mapping (Speight, 2001). In such procedures, properties of feedstock are mapped to show characteristics that are in visual form rather than in tabular form. In this manner the visual characteristics
of the feedstock are used to evaluate and predict the behavior of the feedstock in various refining scenarios. Whether or not such methods will replace the simpler form of property correlations remains to be determined. It is more than likely that both will continue to be used in a complementary fashion for some time to come. However, there is also the need to recognize that what is adequate for one refinery and one feedstock (or feedstock blend provided that the blend composition does not change significantly) will not be suitable for a different refinery with a different feedstock (or feedstock blend).

One of the most effective means of feedstock mapping has arisen though the use of a multidisciplinary approach that involves use of all of the necessary properties of a feedstock. However, it must be recognized that such maps do not give any indication of the complex interactions that occur between, for example, such fractions as the asphaltenes and resins (Koots and Speight, 1975; Speight, 1994), but it does allow predictions of feedstock behavior. It must also be recognized that such a representation varies for different feedstocks.

More recent work related to feedstock mapping has involved the development of a different type of compositional map using the molecular weight distribution and the molecular type distribution as coordinates. Such a map can provide insights into many separation and conversion processes used in petroleum refining (Speight, 2001).

Thus a feedstock map can be used to show where a particular physical or chemical property tends to concentrate on the map. For example, the coke-forming propensity, that is, the amount of the carbon residue, is shown for various regions on the map for a sample of atmospheric residuum (Fig. 2.7; Long and Speight, 1998). In addition, a feedstock map can be very useful for predicting the effectiveness of various types of separations processes as applied to petroleum (Fig. 2.8; Speight, 2001).

In contrast to the cut lines generated by separation processes, conversion processes move materials in the composition from one molecular type to another. For example, reforming converts saturates to aromatics and hydrogenation converts aromatic molecules to saturated molecules and polar aromatic molecules to either aromatic molecules or saturated molecules (Fig. 2.9; Speight, 2001). The processes illustrated are reforming, hydrogenation, hydrotreating, hydrocracking, visbreaking, and heat soaking. The arrows go from the material converted to what it is converted to. Hydrotreating removes nitrogen and sulfur compounds from polar aromatics without much change in molecular weight. Hydrocracking converts polar species to aromatics while at the same time reducing molecular weight. Visbreaking and heat soaking primarily lower or raise the molecular weight of the polar species in the composition map. Thus visbreaking is used to lower the viscosity of heavy oils, whereas heat soaking is a coking
Figure 2.7. Map for fractional separation of petroleum

Figure 2.8. Separation processes from a petroleum map
method. Thus conversion processes can change the shape and size of the composition map.

Thus the data derived from any one or more of the analytical methods described in this chapter can be combined to give an indication of the characteristics of the feedstock as well as options for feedstock processing and for the prediction of product properties.

Indeed, the use of physical properties for feedstock evaluation has continued in refineries and in process research laboratories to the present time and will continue for some time. It is, of course, a matter of choosing the relevant and meaningful properties to meet the nature of the task. What is certain is that the use of one single property cannot accurately portray the character and behavior of petroleum.

REFERENCES


