9 Petroleum Analysis

9.1 INTRODUCTION

Petroleum exhibits a wide range of physical properties and several relationships can be made between various physical properties (Speight, 2001). Whereas properties such as **viscosity**, **density**, **boiling point**, and color of petroleum may vary widely, the ultimate or elemental analysis varies, as already noted, over a narrow range for a large number of petroleum samples. The carbon content is relatively constant, while the hydrogen and heteroatom contents are responsible for the major differences between petroleum samples. Coupled with the changes brought about to the feedstock constituents by refinery operations, it is not surprising that petroleum characterization is a monumental task.

Petroleum refinery processes can be conveniently divided into three different types (Chapter 14 and Chapter 15):

1. Separation: division of the feedstock into various streams (or fractions) depending on the nature of the crude material
2. Conversion: that is, the production of saleable materials from the feedstock by skeletal alteration, or even by alteration of the chemical type of the feedstock constituents
3. Finishing: purification of the various product streams by a variety of processes that remove impurities from the product

In some case, a fourth category can be added and includes processes such as the **reforming** (molecular rearrangement) processes. For the purposes of this text, reforming processes are included in the finishing processes because that is precisely what they are: processes designed to finish various refinery streams and render them ready for sale as defined products.

The separation and finishing processes may involve distillation or treatment with a *wash* solution. The conversion processes are usually regarded as those processes that change the number of carbon atoms per molecule (thermal decomposition), alter the molecular hydrogen–carbon ratio (**aromatization**, **hydrogenation**), or even change the molecular structure of the material without affecting the number of carbon atoms per molecule (**isomerization**) (Chapter 15).

Although it is possible to classify refinery operations using the three general terms just outlined, the behavior of various feedstocks in these refinery operations is not simple. The atomic ratios from ultimate analysis give an indication of the nature of a feedstock and the generic hydrogen requirements to satisfy the refining chemistry (Chapter 15), but it is not possible to predict with any degree of certainty how the feedstock will behave during refining. Any deductions made from such data are pure speculation and are open to much doubt.

The chemical composition of a feedstock is a much truer indicator of refining behavior. Whether the composition is represented in terms of compound types or in terms of generic compound classes, it can enable the refiner to determine the nature of the reactions. Hence, chemical composition can play a large part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed (Nelson, 1958; Ali et al., 1985; Wallace et al., 1988).

As indicated elsewhere (Chapter 7, Chapter 8, and Chapter 11), petroleum is an exceedingly complex and structured mixture consisting predominantly of hydrocarbons and containing sulfur, nitrogen, oxygen, and metals as minor constituents. Although sulfur has been reported in elemental form in some crude oils, most of the minor constituents occur in combination with carbon and hydrogen.

The physical and chemical characteristics of crude oils and the yields and properties of products or fractions prepared from them vary considerably and are dependent on the concentration of the various types of hydrocarbons and minor constituents present. Some types of petroleum have economic advantages as sources of fuels and lubricants with highly restrictive characteristics because they require less specialized processing than that needed for production of the same products from many types of crude oil. Others may contain unusually low concentrations of components that are desirable fuel or lubricant constituents, and the production of these products from such crude oils may not be economically feasible.

Evaluation of petroleum for use as a feedstock usually involves an examination of one or more of the physical properties of the material. By this means, a set of basic characteristics can be obtained that can be correlated with utility. To satisfy specific needs with regard to the type of petroleum to be processed, as well as to the nature of the product, various standards organizations, such as the American Society for Testing and Materials in North America and the Institute of Petroleum in Britain, have devoted considerable time and effort to the correlation and standardization of methods for the inspection and evaluation of petroleum and petroleum products. A complete discussion of the large number of routine tests available for petroleum fills an entire book. However, it seems appropriate that in any discussion of the physical properties of petroleum and petroleum products reference be made to the corresponding test, and accordingly, the various test numbers have been included in the text.

9.2 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 assure adequate (correct) sampling by use of the prescribed protocols (ASTM D4057).

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 if 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 and these are: (1) an inspection assay and (2) a comprehensive assay (Table 9.1).

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 if 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

TABLE 9.1
Recommended Inspection Data Required for Petroleum and Heavy Feedstocks (Including Residua)

Petroleum	Heavy Feedstocks
Density, specific gravity	Density, specific gravity
API gravity	API gravity
Carbon, wt.%	Carbon, wt.%
Hydrogen, wt.%	Hydrogen, wt.%
Nitrogen, wt.%	Nitrogen, wt.%
Sulfur, wt.%	Sulfur, wt.%
	Nickel, ppm
	Vanadium, ppm
	Iron, ppm
Pour point	Pour point
Wax content	
Wax appearance temperature	
Viscosity (various temperatures)	Viscosity (various temperatures)
Carbon residue of residuum	Carbon residue
	Ash, wt.%
Distillation profile:	Fractional composition:
All fractions plus vacuum residue	Asphaltenes, wt.%
	Resins, wt.%
	Aromatics, wt.%
	Saturates, wt.%

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 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. A full petroleum assay may involve at least determinations of (1) carbon residue yield, (2) density (**specific gravity**), (3) sulfur content, (4) distillation profile (volatility), (5) metallic constituents, (6) viscosity, and (7) pour point, as well as any tests designated necessary to understand the properties and behavior of the crude oil under examination.

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 D323, IP 69, IP 402), (2) total acid number—(ASTM D664, IP 177), and **the aniline point** (or mixed aniline point) (ASTM D611, IP 2).

The **Reid vapor pressure** test method (ASTM D323, IP 69) measures the vapor pressure of volatile petroleum. The Reid vapor pressure differs from the true vapor pressure of the sample due to 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