Handbook of Petroleum Product Analysis

JAMES G. SPEIGHT

A JOHN WILEY & SONS, INC., PUBLICATION

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data is available:

ISBN: 0-471-20346-7

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

PREFACE

This book complements the book *Handbook of Petroleum Analysis* (J.G. Speight, John Wiley & Sons, 2001), and it is the purpose of these books to make available, in two handy volumes the essential elements of all analytical tests used to characterize petroleum and petroleum products.

It is, of course, critical for testing laboratory personnel to be fully familiar with all the details of the tests they are performing. But it is also important for nonlaboratory personnel to know at least the significance, advantages, and limitations of particular tests used to characterize product quality. Both the suppliers and the customers need to agree on the appropriate product quality specifications, and this can be achieved by understanding the intricacies of the respective test methods.

Product specifications not based on realistic testing capabilities can only lead to quality complaints and unhappiness on the part of both suppliers and customers. Therefore, we expect that this book will prove useful not only to laboratory personnel but also to product specification writers, process engineers, process scientists, researchers, and marketing staff in understanding the importance of these tests as well as their limitations, so that sound conclusions can be reached regarding the quality and performance of a particular product.

Organizations such as the American Society for Testing and Materials (ASTM) in the United States, the Institute of Petroleum (IP, London, U.K.), the Association Française de Normalisation (AFNOR, Paris, France), the Deutsche Institut für Normung (DIN, Germany), the Japan Industrial Standards (JIS, Tokyo, Japan), and the International Organization for Standardization (ISO, Geneva, Switzerland) have made significant contributions in developing standard test methods for the analyses of petroleum products. Although it is not possible to include all of the test methods of these organizations, cross-reference is made of the standard methods of analysis of the ASTM to those that are known for the IP.

In addition, the ASTM has discontinued several of the tests cited in the text for testing and materials, but they are included here because of their continued use by analytical laboratories. Several tests may even have been modified for internal company use, and there is no way of authenticating such use. Indeed, many tests should be adopted for internal company use

instead of existing in-house testing protocols. For example, one might read in the published literature of the use of modified naphtha to precipitate an asphaltene fraction. Such a statement is meaningless without precise definition of the chemical composition of the modified naphtha. Naphtha is a complex petroleum product that can vary depending on the method of production. So, without any qualification or chemical description of the modified naphtha, a comparison of the precipitate with a pentane-asphaltene or heptane-asphaltene will be futile. Indeed, cross-comparisons within the in-house laboratories may be difficult if not impossible. The moral of this tale is that testing protocols *should* be standardized!

It is not intented that this book should replace the *Annual Book of ASTM Standards*. This book is intended to be a complementary volume that contains explanations of the *raison d'être* of the various test methods.

Each chapter is written as a stand-alone unit, which has necessitated some repetition. This repetition is considered necessary for the reader to have all of the relevant information at hand, especially where there are tests that can be applied to several products. Where this is not possible, cross-references to the pertinent chapter(s) are included. Several general references are listed for the reader to consult for a more detailed description of petroleum products. No attempt has been made to be exhaustive in the citations of such works. Thereafter, the focus is to cite the relevant test methods that are applied to petroleum products.

Finally, in this book, no preference is given to any particular tests. All lists of tests are alphabetical.

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CHAPTER

1

PETROLEUM ANALYSIS

1.1. INTRODUCTION

Petroleum, meaning literally "rock oil," is the term used to describe a myriad of hydrocarbon-rich fluids that have accumulated in subterranean reservoirs. Petroleum (also called *crude oil*) varies dramatically in color, odor, and flow properties that reflect the diversity of its origin (Table 1.1).

Petroleum products are any petroleum-based products that can be obtained by refining (Chapter 2) and comprise refinery gas, ethane, liquefied petroleum gas (LPG), naphtha, gasoline, aviation fuel, marine fuel, kerosene, diesel fuel, distillate fuel oil, residual fuel oil, gas oil, lubricants, white oil, grease, wax, asphalt, as well as coke. Petrochemical products (Speight, 1999a) are not included here.

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

Crude petroleum and the products obtained therefrom contain a variety of compounds, usually but not always hydrocarbons. As the number of carbon atoms in, for example, the paraffin series increases, the complexity of petroleum mixtures also rapidly increases. Consequently, detailed analysis of the individual constituents of the higher boiling fractions becomes increasingly difficult, if not impossible.

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

Table 1.1. Illustration of the Variation in Composition (Residuum Content) and Properties (Specific Gravity and API Gravity) of Petroleum

Crude Oil	Specific Gravity	API Gravity	Residuum > 1000°F
U.S. Domestic			
California	0.858	33.4	23.0
Oklahoma	0.816	41.9	20.0
Pennsylvania	0.800	45.4	2.0
Texas	0.827	39.6	15.0
Texas	0.864	32.3	27.9
Foreign			
Bahrain	0.861	32.8	26.4
Iran	0.836	37.8	20.8
Iraq	0.844	36.2	23.8
Kuwait	0.860	33.0	31.9
Saudi Arabia	0.840	37.0	27.5
Venezuela	0.950	17.4	33.6

These general definitions of the different fractions are subject to the many combinations of the hydrocarbon types (Speight, 1999a; Speight, 2001) and the action of the adsorbent or the solvent used in the separation procedure. For example, a compound containing one benzenoid ring (six aromatic carbon atoms) that has 12 nonaromatic carbons in alkyl side chains can be separated as an aromatic compound depending on the adsorbent employed.

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

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

variations in temperature and pressure to which the precursors were subjected.

Thus the purely hydrocarbon content may be higher than 90% by weight for paraffinic petroleum and 50% by weight for heavy crude oil and much lower for tar sand bitumen. The nonhydrocarbon constituents are usually concentrated in the higher-boiling portions of the crude oil. The carbon and hydrogen content is approximately constant from crude oil to crude oil even though the amounts of the various hydrocarbon types and of the individual isomers may vary widely. Thus the carbon content of various types of petroleum is usually between 83% and 87% by weight and the hydrogen content is in the range of 11–14% by weight.

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

Measurements of bulk properties are generally easy to perform and, therefore, quick and economical. Several properties may correlate well with certain compositional characteristics and are widely used as a quick and inexpensive means to determine those characteristics. The most important properties of a whole crude oil are its boiling-point distribution, its density (or API gravity), and its viscosity. The *boiling-point distribution*, *boiling profile*, or *distillation assay* gives the yield of the various distillation cuts, and selected properties of the fractions are usually determined (Table 1.2). It is a prime property in its own right that indicates how much gasoline and other transportation fuels can be made from petroleum without conversion. Density and viscosity are measured for secondary reasons. The former helps to estimate the paraffinic character of the oil, and the latter permits the assessment of its undesirable residual material that causes resistance to flow. Boiling-point distribution, density, and viscosity are easily measured and give a quick first evaluation of petroleum oil. Sulfur content, another crucial and primary property of a crude oil, is also readily determined. Certain composite characterization values, calculated from density and mid-boiling point, correlate better with molecular composition than density alone (Speight, 2001).

The acceptance of heavy oil and bitumen as refinery feedstocks has meant that the analytical techniques used for the lighter feedstocks have had to evolve to produce meaningful data that can be employed to assist in defining refinery scenarios for processing the feedstocks. In addition, selection of the most appropriate analytical procedures will aid in the predictability of feedstock behavior during refining. This same rationale can also be applied to feedstock behavior during recovery operations. Indeed,

Table 1.2. Distillation Profile of Petroleum (Leduc, Woodbend, Upper Devonian, Alberta, Canada) and Selected Properties of the Fractions

	Boiling range °C	Boiling range °F	Wt. %	Wt. % Cumulative	Specific Gravity	API Gravity	Sulfur Wt. %	Carbon Residue (Conradson)
Whole Crude Oil				100.0	0.828	39.4	0.4	1.5
Fraction*								
1	0–50	0–122	2.6	2.6	0.650	86.2		
2	50–75	122–167	3.0	5.6	0.674	78.4		
3	75–100	167–212	5.2	10.8	0.716	66.1		
4	100–125	212–257	6.6	17.4	0.744	58.7		
5	125–150	257–302	6.3	23.7	0.763	54.0		
6	150–175	302–347	5.5	29.2	0.783	49.2		
7	175–200	347–392	5.3	34.5	0.797	46.0		
8	200–225	392–437	5.0	39.5	0.812	42.8		
9	225–250	437–482	4.7	44.2	0.823	40.4		
10	250–275	482–527	6.6	50.8	0.837	37.6		
11	<200	<392	5.4	56.2	0.852	34.6		
12	200–225	392–437	4.9	61.1	0.861	32.8		
13	225–250	437–482	5.2	66.3	0.875	30.2		
14	250–275	482–527	2.8	69.1	0.883	28.8		
15	275–300	527–572	6.7	75.4	0.892	27.0		
Residuum	>300	>572	22.6	98.4	0.929	20.8		6.6
Distillation loss				1.6				

*Distillation at 765 mm Hg then at 40 mm Hg for fractions 11–15.

bitumen, a source of synthetic crude oil, is so different from petroleum (Speight and Moschopedis, 1979; Speight, 1990, Speight, 1999a, Speight, 2001) that many of the test methods designed for petroleum may need modification (Wallace, 1988).

Thus knowledge of the composition of petroleum allows the refiner to optimize the conversion of raw petroleum into high-value products. Petroleum is now the world's main source of energy and petrochemical feedstock. Originally, petroleum was distilled and sold as fractions with desirable physical properties. Today crude oil is sold in the form of gasoline, solvents, diesel and jet fuel, heating oil, lubricant oils, and asphalts, or it is converted to petrochemical feedstocks such as ethylene, propylene, the butenes, butadiene, and isoprene. These feedstocks are important, because they form the basis for, among others, the plastics, elastomer, and artificial fiber industries. Modern refining uses a sophisticated combination of heat, catalyst, and hydrogen to rearrange the petroleum molecules into these products. Conversion processes include coking, hydrocracking, and catalytic cracking to break large molecules into smaller fractions; hydrotreating to reduce heteroatoms and aromatics, creating environmentally acceptable products; and isomerization and reforming to rearrange molecules into those with high value, e.g., gasoline with a high octane number.

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

In addition, knowledge of the composition of petroleum allows the geochemist to answer questions of precursor-product relationships and conversion mechanisms. Biomarkers, molecules that retain the basic carbon skeletons of biological compounds from living organisms after losing functional groups through the maturation process, play an important role in such studies. The distribution of biomarker isomers can not only serve as fingerprints for oil/oil and oil/source correlation (to relate the source and reservoir) but also give geochemical information on organic source input (marine, lacustrine, or land-based sources), age, maturity, depositional environment (for example, clay or carbonate, oxygen levels, salinity), and alteration (for example, water washing, biodegradation).

The need for the application of analytical techniques has increased over the past three decades because of the change in feedstock composition. This has arisen because of the increased amounts of the heavier feedstocks that

are now used to produce liquid products. Before the energy crises of the 1970s, the heavier feedstocks were used infrequently as sources of liquid fuels and were used to produce asphalt. Now these feedstocks have increased in value as sources of liquid fuels.

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

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

1.2. DEFINITIONS

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

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

Historically, physical properties such as boiling point, density (gravity), odor, and viscosity have been used to describe oils. Petroleum may be called *light* or *heavy* in reference to the amount of low-boiling constituents and the relative density (specific gravity). Likewise, odor is used to distinguish between *sweet* (low sulfur) and *sour* (high sulfur) crude oil. Viscosity indicates the ease of (or more correctly the resistance to) flow.

However, where there is the need for a thorough understanding of petroleum and the associated technologies, it is essential that the definitions and the terminology of petroleum science and technology be given prime consideration (Speight, 1999a). This presents a better understanding of petroleum, its constituents, and its various fractions. Of the many forms of terminology that have been used not all have survived, but the more com-

monly used are illustrated here. Particularly troublesome, and more confusing, are those terms that are applied to the more viscous materials, for example, the use of the terms *bitumen* and *asphalt*. This part of the text attempts to alleviate much of the confusion that exists, but it must be remembered that the terminology of petroleum is still open to personal choice and historical usage.

Petroleum is a naturally occurring mixture of hydrocarbons, generally in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements (ASTM D-4175, 1998; Speight, 1999a, 1999b and references cited therein).

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

Crude petroleum is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation (Speight, 1999a, Speight, 2001). The terminology of these fractions has been bound by utility and often bears little relationship to composition.

The molecular boundaries of petroleum cover a wide range of boiling points and carbon numbers of hydrocarbon compounds and other compounds containing nitrogen, oxygen, and sulfur, as well as metallic (porphyrin) constituents. However, the actual boundaries of such a *petroleum map* can only be arbitrarily defined in terms of boiling point and carbon number (Fig. 1.1). In fact, petroleum is so diverse that materials from different sources exhibit different boundary limits, and for this reason alone it is not surprising that petroleum has been difficult to *map* in a precise manner (Speight, 2001).

Because there is a wide variation in the properties of crude petroleum, the proportions in which the different constituents occur vary with origin (Gruse and Stevens, 1960; Speight, 1999a). Thus some crude oils have higher proportions of the lower-boiling components and others (such as heavy oil and bitumen) have higher proportions of higher-boiling components (asphaltic components and residuum).

There are several other definitions that also must be included in any text on petroleum analysis, in particular because this text also focuses on the

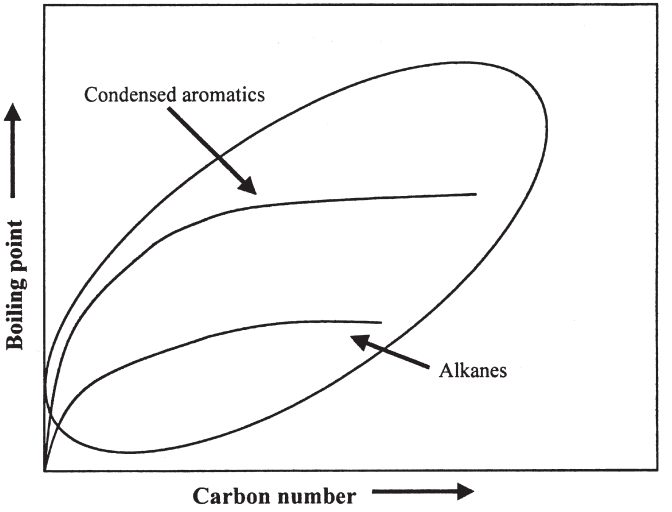

Figure 1.1. Boiling point-carbon number profile for petroleum

analysis of heavy oil and bitumen. These definitions are included because of the increased reliance on the development of these resources and the appearance of the materials in refineries.

Heavy oil (heavy crude oil) is more viscous than conventional crude oil and has a lower mobility in the reservoir but can be recovered through a well from the reservoir by the application of secondary or enhanced recovery methods. On the other hand, *tar sand* includes the several rock types that contain an extremely viscous hydrocarbonaceous material that is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques.

More descriptively, *tar sand* is an unconsolidated-to-consolidated sandstone or a porous carbonate rock, impregnated with bitumen. In simple terms, an unconsolidated rock approximates the consistency of dry or moist sand, and a consolidated rock may approximate the consistency of set concrete. Alternative names, such as *bituminous sand* or (in Canada) *oil sand*, are gradually finding usage, with the former name more technically correct. The term *oil sand* is also used in the same way as the term *tar sand*, and the terms are used interchangeably. The term *oil sand* is analogous to the term *oil shale*. Neither material contains oil, but oil is produced therefrom by application of thermal decomposition methods. It is important to understand that tar sand and the bitumen contained therein are different components of the deposit. The recovery of the bitumen, a hydrocarbonaceous material that can be converted into *synthetic crude oil* (Speight, 1990,

Speight, 1999a), depends to a large degree on the composition and construction of the sands.

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

The term *bitumen* (also, on occasion, referred to as *native asphalt* and *extra heavy oil*) includes a wide variety of reddish-brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight. *Bitumen* is frequently found filling pores and crevices of sandstone, limestone, or argillaceous sediments, in which case the organic and associated mineral matrix is known as *rock asphalt*.

On the basis of the definition of tar sand (above), *bitumen* is a naturally occurring hydrocarbonaceous material that has little or no mobility under reservoir conditions and which cannot be recovered through a well by conventional oil well production methods including currently used enhanced recovery techniques; current methods for bitumen recovery involve mining (Speight, 1990).

Because of the immobility of the bitumen, the permeability of the deposit is low and passage of fluids through the deposit is prevented. Bitumen is a high-boiling material with little, if any, material boiling below 350°C (660°F), and the boiling range approximates the boiling range of an atmospheric residuum and has a much lower proportion of volatile constituents than a conventional crude oil (Speight, 1999a, Speight, 2001).

Synthetic crude oil is the *hydrocarbon* liquid that is produced from *bitumen*, by a variety of processes that involve thermal decomposition. *Synthetic crude oil* (also referred to as *syncrude*) is a marketable and transportable product that resembles conventional crude oil. *Synthetic crude oil*, although it may be produced from one of the less conventional fossil fuel sources, can be accepted into and refined by the usual refinery system.

For the purposes of terminology, it is preferable to subdivide petroleum and related materials into three major subgroups (Table 1.3; Speight, 1999a):

1. Materials that are of natural origin;
2. Materials that are manufactured; and
3. Materials that are integral fractions derived from the natural or manufactured products.

Table 1.3. Subdivision of Fossil Fuels Into Various Subgroups

Natural Materials	Derived Materials	Manufactured Materials
Natural gas	Saturates	Synthetic crude oil
Petroleum	Aromatics	Distillates
Heavy oil	Resins	Lubricating oils
Bitumen*	Asphaltenes	Wax
Asphaltite	Carbenes**	Residuum
Asphaltoid	Carboids**	Asphalt
Ozocerite (natural wax)	Asphaltols***	Coke
Kerogen		Tar
Coal		Pitch

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

The natural materials occur in different locations throughout the Earth. The derived and manufactured materials are obtained by using methods different from those used to obtain the natural materials.

1.3. HISTORICAL PERSPECTIVES

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

The *history* of any subject is the means by which the subject is studied in the hope that much can be learned from the events of the past. In the current context, the occurrence and use of petroleum, petroleum derivatives (naphtha), heavy oil, and bitumen is not new. The use of petroleum and its derivatives was practiced in pre-common era times and is known largely through historical use in many of the older civilizations (Henry, 1873; Abraham, 1945; Forbes, 1958a, 1958b, 1959, 1964; James and Thorpe, 1994). Thus the use of petroleum and the development of related technology is not such a modern subject as we are inclined to believe. The petroleum industry is essentially a twentieth-century industry, but to understand the evolution of the industry, it is essential to have a brief understanding of the first uses of petroleum.

Briefly, petroleum and bitumen have been used for millennia. For example, the Tigris–Euphrates valley, in what is now Iraq, was inhabited as early as 4000 B.C. by the people known as the Sumerians, who established one of the first great cultures of the civilized world. The Sumerians devised the cuneiform script, built the temple-towers known as ziggurats, and developed an impressive code of law, literature, and mythology. As the culture developed, *bitumen* or *asphalt* was frequently used in construction and in ornamental works.

Although it is possible to differentiate between the words *bitumen* and *asphalt* in modern use (Speight, 1999a) the occurrence of these words in older texts offers no such possibility. It is significant that the early use of bitumen was in the nature of cement for securing or joining together various objects, and it thus seems likely that the name itself was expressive of this application.

Early references to petroleum and its derivatives occur in the Bible, although by the time the various books of the Bible were written, the use of petroleum and bitumen was established. Investigations at archeological sites have confirmed the use of petroleum and bitumen in antiquity for construction, mummification, decorative jewelry, waterproofing, as well as for medicinal use (Speight, 1978, 1999a). Many other references to bitumen are found throughout the Greek and Roman empires, and from that time to the Middle Ages early scientists (alchemists) frequently referred to the use of bitumen. In the late fifteenth and early sixteenth centuries both Christopher Columbus and Sir Walter Raleigh have been credited with the discovery of the asphalt deposit on the island of Trinidad and apparently used the material to caulk their ships. There was also an interest in the thermal product of petroleum (nafta; naphtha) when it was discovered that this material could be used as an illuminant and as a supplement to asphalt incendiaries in warfare.

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

Thus the history of analysis of petroleum and its products can only be suggested to have started during the second half of the nineteenth century. For example, in 1857 several aromatic hydrocarbons from Burma petroleum were identified by the formation of the barium salts of benzenesul-

fonic acids followed by fractional crystallization. In addition, an analytical distillation of petroleum was carried out in the early 1870s (Silliman, 1872). Further developments of the analytical chemistry of petroleum continued throughout the century (Mair, 1960).

It might be assumed that petroleum analysis evolved as analytical chemistry evolved. And it is correct to ascribe to analytical chemistry a position of primary importance because only through chemical analysis can matter (in this context, petroleum) in its variety of forms be dealt with logically.

1.4. MODERN PERSPECTIVES

The modern petroleum industry began in 1859 with the discovery and subsequent commercialization of petroleum in Pennsylvania (Bell, 1945). During the 6,000 years of its use, the importance of petroleum has progressed from the relatively simple use of asphalt from Mesopotamian seepage sites to the present-day refining operations that yield a wide variety of products and petrochemicals (Speight, 1999a). However, what is more pertinent to the industry is that throughout the millennia in which petroleum has been known and used, it is only in the twentieth century that attempts were made to formulate and standardize petroleum analysis.

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

Spectrophotometers came into widespread use beginning around 1940, and this led to wide application in petroleum analysis. *Ultraviolet absorption spectroscopy*, *infrared spectroscopy*, *mass spectrometry*, *emission spectroscopy*, and *nuclear magnetic resonance spectroscopy* continue to make major contributions to petroleum analysis.

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

The foregoing section is included to introduce the reader to the historical aspects of petroleum analysis and to show the glimmerings of how it evolved over the twentieth century. Indeed, despite the historical use of petroleum and related materials, the petroleum industry is a modern industry, having come into being in 1859. From these comparatively recent beginnings, petroleum analysis has arisen as a dedicated science.

1.5. ANALYSIS AND SPECIFICATIONS

Petroleum exhibits wide variations in composition and properties, and these occur not only in petroleum from different fields but also in oils taken from different production depths in the same well. Historically, physical properties such as boiling point, density (gravity), and viscosity have been used to describe petroleum, but the needs for analysis are even more extensive (Table 1.4).

Table 1.4. Analytical Inspections Required for Petroleum, Heavy Oil, and 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 and at reservoir temperature)
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. %

* Conradson carbon residue or microcarbon residue.

Petroleum analysis involves not only determining the composition of the material under investigation but, more appropriately, determining the suitability of the petroleum for refining or the product for use. In this sense, the end product of petroleum analysis or (testing) is a series of data that allow the investigator to *specify* the character and quality of the material under investigation. Thus a series of specifications are determined for petroleum and its products.

Because of the differences in petroleum composition, the importance of the correct sampling of crude oil that contains light hydrocarbons cannot be overestimated. Properties such as specific gravity, distillation profile, vapor pressure, hydrogen sulfide content, and octane number of gasoline are affected by the light hydrocarbon content so that suitable cooling or pressure sampling methods must be used and care taken during the subsequent handling of the oil to avoid the loss of any volatile constituents. In addition, adequate records of the circumstances and conditions during sampling must be made. For example, sampling from oil field separators, the temperatures and pressures of the separation plant, and the atmospheric temperature should be noted.

Hence, the production of data focuses on (1) measurement, 2) accuracy, (3) precision, and (4) method validation, all of which depend on the sampling protocols that were used to obtain the sample. Without strict sampling protocols, variation and loss of accuracy (or precision) must be anticipated. For example, correct sampling of the product in storage or carrier tanks is important to obtain a representative sample for the laboratory tests that are essential in converting measured quantities to the standard volume.

Elemental analyses of petroleum show that it contains mainly carbon and hydrogen. Nitrogen, oxygen, and sulfur (heteroelements) are present in smaller amounts, and trace elements such as vanadium, nickel, etc, are also present. Of the heteroelements, sulfur is the most important. 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. The attempted classification of crude oils in terms of these three main structural types has proved inadequate.

The value of a particular crude to a refiner depends on its quality and whether he can economically obtain a satisfactory product pattern that matches market demand (*market pull*). In the main, the refiner is not concerned with the actual chemical nature of the material but in methods of analysis that would provide information sufficient to assess the potential quality of the oil, to supply preliminary engineering data, and also to indicate whether any difficulties might arise in handling, refining, or transporting petroleum or its products. Such information may be obtained in one of two ways:

1. Preliminary assay-inspection data.
2. A full assay involving the preparation of a true boiling point curve and the analysis of fractions and product blends throughout the full range of the crude oil.

The *preliminary assay* provides general data on the oil and is based on simple tests such as distillation range, water content, specific gravity, and sulfur content that enable desirable or undesirable features to be noted. This form of assay requires only a small quantity of sample and is therefore particularly useful for the characterization of oil field samples produced from cores, drill stem tests, or seepages.

The tests in the preliminary assay are relatively simple and can be completed in a short time and generally on a routine basis. This assay gives a useful general picture of the quality of petroleum, but it does not cover the work necessary to provide adequate data, for example, for the design of refinery equipment, nor does it produce a sufficient quantity of the various products from the crude so that they can be examined for quality. A *full assay* of petroleum is based on a true boiling point distillation of the crude, and sufficient data are obtained to assess the yields and properties of the straight-run products, covering light hydrocarbons, light, middle, and heavy distillate, lubricants, residual fuel oil, and residuum. Often, the middle ground is reached between the preliminary assay and the full assay, but the requirements may also be feedstock dependent (Table 1.4).

A *feedstock specification* or *product specification* provides the data that give adequate control of feedstock behavior in a refinery or product quality. Thus a specification offers the luxury of *predictability* of feedstock behavior in a refinery or *predictability* of product quality (therefore, product behavior) relative to market demand. Ultimately, feedstock behavior and/or product quality is judged by an assessment of performance. And it is *performance* that is the ultimate criterion of quality. It is therefore necessary to determine those properties, the values of which can be established precisely and relatively simply by inspection tests in a control laboratory, that correlate closely with the important performance properties.

Sometimes the inspection tests attempt to measure these properties, for example, the carbon residue of a feedstock that is an approximation of the amount of the thermal coke that will be formed during refining or a research octane number test devised to measure performance of motor fuel. In other cases the behavior must be determined indirectly from a series of test results.

In addition, there are many instances in which interrelationships of the specification data enable properties to be predicted from the measured properties with as good precision as can be obtained by a single test. It would be possible to examine in this way the relationships between all the

specified properties of a product and to establish certain key properties from which the remainder could be predicted, but this would be a tedious task.

An alternative approach to that of picking out the essential tests in a specification by using regression analysis is to examine at the specification as a whole and to use the necessary component. This is termed *principal components analysis* (see also p. 23). In this method a set of data as points in *multidimensional* space (*n-dimensional*, corresponding to *n* original tests) is examined to determine the direction that accounts for the biggest variability in the data (*first principal component*). The process is repeated until *n* principal components are evaluated, but it must be determined which components are of practical importance because some principal components may be due to experimental error. The number of significant principal components shows the number of independent properties being measured by the tests considered.

The number of independent properties having been established, there exists a natural basis for making the specification more efficient. In the long term, it might be possible to obtain new tests of a fundamental nature to replace existing tests. In the short term, selecting the best of the existing tests to define product quality will be beneficial.

Finally, the analytical methods used to describe petroleum must be modified for the characterization of tar sand bitumen in the same way that tests for conventional petroleum have been modified and/or replaced by newer, more relevant test methods. For example, what might appear to be a test of minimal value for conventional petroleum might afford invaluable data for determining the behavior of tar sand bitumen or the potential products from each.

In fact, it is because of behavior differences that research into text methods for tar sand bitumen is continuing (Wallace, 1988; Speight, 1999a, Speight, 1999b). Clearly, for maximum efficiency the tests that are specified for any feedstock or product should be as independent of each other as possible. In fact, the efficiency of a specification should be judged by the extent to which the tests specified will:

1. Predict (control) feedstock behavior;
2. Predict (control) and product quality;
3. Measure independent properties;
4. Measure these properties with adequate precision; and
5. Offer rapid response to refinery and laboratory demands.

Petroleum analysis has been greatly augmented in recent years by application of a wide variety of instrumental techniques to studies of the hydro-

carbon composition of crude oils and their products (Speight, 1999a, Speight, 2001). Before this, hydrocarbon type analyses (percent paraffins, naphthenes, olefins, and aromatics) were derived from correlations based on physical data. The advent of instrumental techniques has led to two major developments:

1. Individual component analysis;
2. An extension to, and more detailed subdivision of, the various compound types that occur in the higher-boiling ranges of petroleum distillates.

Of these instrumental techniques, gas/liquid chromatography and mass spectrometry are the most important in providing the hydrocarbon composition data in crude oil assay work. By gas chromatographic analysis, it is now possible to determine routinely the individual methane (CH_4) to heptane (C_7H_{16}) hydrocarbons and the individual aromatics that boil below 165°C (330°F) and also obtain a complete normal paraffin distribution up to C_{50}. In addition, with a microcoulometric detector specific to sulfur, the sulfur compound distribution can be obtained throughout the distillate range. Gas chromatographic analysis can also be used to provide simulated true boiling point (TBP) curves, and developments in preparative scale gas/liquid chromatography have made possible the preparation of fractions in quantities sufficient not only for extensive spectrometric analyses but also for the normal inspection type tests to be undertaken.

Mass spectrometry offers a very rapid method for obtaining hydrocarbon type analyses on a wide range of fractions up to and including heavy gas oils. The information obtained on a routine basis subdivides the hydrocarbons into the various groups. The technique can also be used in conjunction with separation procedures such as gas/liquid chromatography, molecular distillation, thermal diffusion, or selective adsorption to provide more detailed analyses where necessary, even on fractions in the lubricating oil range.

Thus petroleum analysis is a complex subject involving a variety of techniques, some of which have been mentioned above. But no single technique should supercede the other. Petroleum analysis is a complex discipline that needs a multidimensional approach. And the explanation of the data that are obtained requires adequate interpretation.

1.6. SAMPLING

The value of any product is judged by the characteristics of the sample as determined by laboratory tests. The sample used for the test(s) must be rep-

resentative of the bulk material, or data will be produced that are not representative of the material and will, to be blunt, be incorrect no matter how accurate or precise the test method is. In addition, the type and cleanliness of sample containers are important: If the container is contaminated or is made of material that either reacts with the product or is a catalyst, the test results may be wrong.

Thus the importance of the correct sampling of any product destined for analysis should always be overemphasized. Incorrect sampling protocols can lead to erroneous analytical data from which performance of the product in service cannot be accurately deduced. For example, properties such as specific gravity, distillation yield, vapor pressure, hydrogen sulfide content, and octane number of the gasoline are affected by the content of low-boiling hydrocarbons so that suitable cooling or pressure sampling methods must be used and care must be taken during the subsequent handling of the sample to avoid the loss of any volatile components. In addition, adequate records of the circumstances and conditions during sampling must be made; for example, in sampling from storage tanks, the temperatures and pressures of the separation plant and the atmospheric temperature would be noted.

At the other end of the volatility scale, products that contain, or are composed of, high-molecular-weight paraffin hydrocarbons (wax) that are also in a solid state may require judicious heating (to dissolve the wax) and agitation (homogenization, to ensure thorough mixing) before sampling. If room-temperature sampling is the modus operandi and product cooling causes wax to precipitate, homogenization to ensure correct sampling is also necessary.

Representative samples are prerequisite for the laboratory evaluation of any type of product, and many precautions are required in obtaining and handling representative samples (ASTM D-270, ASTM D-1265). The precautions depend on the sampling procedure, the characteristics (low-boiling or high-boiling constituents) of the product being sampled, and the storage tank, container, or tank carrier from which the sample is obtained. In addition, the sample container must be clean, and the type to be used depends not only on the product but also on the data to be produced.

The basic objective of each procedure is to obtain a truly representative sample or, more often, a composite of several samples that can be considered to be a representative sample. In some cases, because of the size of the storage tank and the lack of suitable methods of agitation, several samples are taken from large storage tanks in such a manner that the samples represent the properties of the bulk material from different locations in the tank and thus the composite sample will be representative of the entire lot being sampled. This procedure allows for differences in sample that might result from the stratification of the bulk material because of tank size or

temperature at the different levels of the storage tank. Solid samples require a different protocol that might involve melting (liquefying) of the bulk material (assuming that thermal decomposition is not induced) followed by homogenization. On the other hand, the protocol used for coal sampling (ASTM D-346, ASTM D-2013) might also be applied to sampling of petroleum products, such as coke, that are solid and for which accurate analysis is required before sale.

Once the sampling procedure is accomplished, the sample container should be labeled immediately to indicate the product, time of sampling, location of the sampling point, and any other information necessary for the sample identification. And, if the samples were taken from different levels of the storage tank, the levels from which the samples were taken and the amounts taken and mixed into the composite should be indicated on the sample documentation.

Although the above text is focused on the acquisitions of samples from storage tanks, sampling records for any procedure must be complete and should include, but are not restricted to, information such as:

1. The precise (geographic or other) location (or site or refinery or process) from which the sample was obtained.
2. The identification of the location (or site or refinery or process) by name.
3. The character of the bulk material (solid, liquid, or gas) at the time of sampling.
4. The means by which the sample was obtained.
5. The protocols that were used to obtain the sample.
6. The date and the amount of sample that was originally placed into storage.
7. Any chemical analyses (elemental analyses, fractionation by adsorbents or by liquids, functional type analyses) that have been determined to date.
8. Any physical analyses (API gravity, viscosity, distillation profile) that have been determined to date.
9. The date of any such analyses included in items 5 and 6.
10. The methods used for analyses that were employed in items 5 and 6.
11. The analysts who carried out the work in items 5 and 6.
12. A log sheet showing the names of the persons (with the date and the reason for the removal of an aliquot) who removed the samples from storage and the amount of each sample (aliquot) that was removed for testing.

In summary, there must be a means of identifying the sample history as carefully as possible so that each sample is tracked and defined in terms of source and activity.

Thus the accuracy of the data from any subsequent procedures and tests for which the sample is used will be placed beyond a *reasonable doubt*.

1.7. MEASUREMENT

The issues that face petroleum analysts include the need to provide higher-quality results. In addition, environmental regulations may influence the method of choice. Nevertheless, the method of choice still depends to a large extent on the boiling range (or carbon number) of the sample to be analyzed. For example, there is a large variation in the carbon number range and boiling points (of normal paraffins) for some of the more common petroleum products and thus a variation in the methods that may be applied to these products (Speight, 2001).

The predominant methods of measuring the properties of petroleum products are covered by approximately seven test methods that are used in the determination of bulk quantities of liquid petroleum and its products (ASTM D-96, ASTM D-287, ASTM D-1085, ASTM D-1086, ASTM D-1087, ASTM D-1250, ASTM D-1298).

Testing for suspended water and sediment (ASTM D-96) is used primarily with fuel oils, where appreciable amounts of water and sediment may cause fouling of facilities for handling the oil and give trouble in burner mechanisms. Three standard methods are available for this determination. The centrifuge method gives the total water and sediment content of the sample by volume, the distillation method gives the water only, volumetrically, and the extraction method gives the solid sediment in percentage by weight.

The determination of density of specific gravity (ASTM D-287, ASTM D-1298) in the measurement and calculation of volume of petroleum products is important because gravity is an index of the weight of a measured volume of the product. Two scales are in use in the petroleum industry, specific gravity and API gravity, the determination being made in each case by means of a hydrometer of constant weight displacing a variable volume of oil. The reading obtained depends on both the gravity and the temperature of the oil.

Gauging petroleum products (ASTM D-1085, discontinued in 1996 but still in use) involves the use of procedures for determining the liquid contents of tanks, ships and barges, tank cars, and tank trucks. Depth of liquid is determined by gauging through specified hatches or by reading gauge

glasses or other devices. There are two basic types of gauges, innage and outage. The procedures used depend on the type of tank to be gauged, its equipment, and the gauging apparatus.

An innage gauge is the depth of liquid in a tank measured from the surface of the liquid to the tank bottom or to a datum plate attached to the shell or bottom. The innage gauge is used directly with the tank calibration table and the temperature of the product to calculate the volume of the product (ASTM D-1250). On the other hand, an outage gauge is the distance between the surface of the product in the tank and the reference point above the surface, which is usually located in the gauging hatch. The outage gauge is used either directly or indirectly with the tank calibration table and the temperature of the product to calculate the volume of product. The amount of any free water and sediment in the bottom of the tank is also gauged so that corrections can be made when calculating the net volume of the crude oil or petroleum product.

The liquid levels of products that have a Reid vapor pressure of 40 lb or more are generally determined by the use of gauge glasses, rotary or slip-tube gauges, tapes and bobs through pressure locks, or other types of gauging equipment. The type of gauging equipment depends on the size and type of the pressure tank.

There are also procedures for determining the temperatures of petroleum and its products when in a liquid state. Temperatures are determined at specified locations in tanks, ships and barges, tank cars, and tank trucks. For a nonpressure tank, a temperature is obtained by lowering a tank thermometer of proper range through the gauging hatch to the specified liquid level. After the entire thermometer assembly has had time to attain the temperature of the product, the thermometer is withdrawn and read quickly. This procedure is also used for low-pressure tanks equipped with gauging hatches or standpipes and for any pressure tank that has a pressure lock. For tanks equipped with thermometer wells, temperatures are obtained by reading thermometers placed in the wells with their bulbs at the desired tank levels. If more than one temperature is determined, the average temperature of the product is calculated from the observed temperatures. Electrical-resistance thermometers are sometimes used to determine both average and spot temperatures.

In general, the volume received or delivered is calculated from the observed gauge readings. Corrections are made for any *free* water and sediment as determined by the gauge of the water level in the tank. The resultant volume is then corrected to the equivalent volume at 15.6°C (60°F) by use of the observed average temperature and the appropriate volume correction table (ASTM D-1250). When necessary, a further correction is made for any suspended water and sediment that may be present in materials such as crude petroleum and heavy fuel oils.

For the measurement of other petroleum products, a wide variety of tests is available. In fact, approximately three hundred and fifty tests (ASTM, 2000) are used to determine the different properties of petroleum products. Each test has its own limits of accuracy and precision that must be adhered to if the data are to be accepted.

1.8. ACCURACY

The *accuracy* of a test is a measure of how close the test result will be to the true value of the property being measured. As such, the accuracy can be expressed as the *bias* between the test result and the true value. However, the *absolute accuracy* can only be established if the true value is known.

In the simplest sense, a convenient method to determine a relationship between two measured properties is to plot one against the other (Fig. 1.2). Such an exercise will provide either a line fit of the points or a spread that may or may not be within the limits of experimental error. The data can then be used to determine the approximate accuracy of one or more points employed in the plot. For example, a point that lies outside the limits of experimental error (a *flyer*) will indicate an issue of accuracy with that test and the need for a repeat determination.

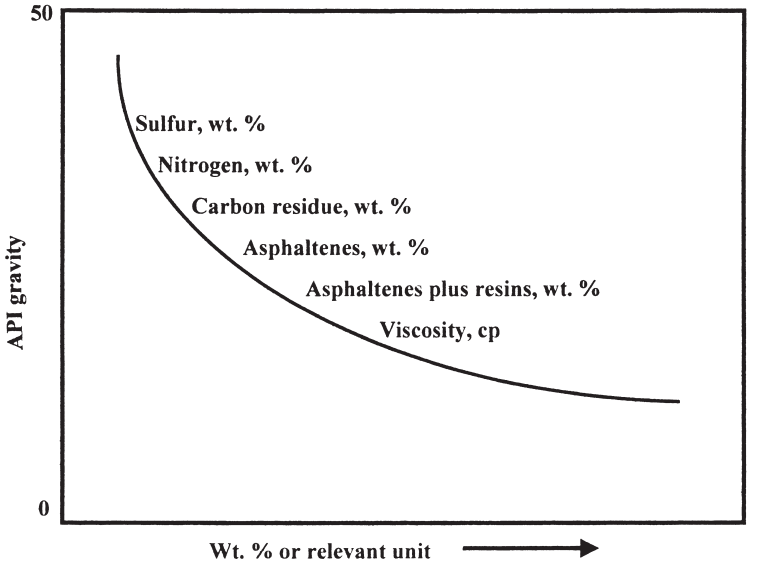

Figure 1.2. Illustration of the general relationship of petroleum properties

However, the graphical approach is not appropriate for finding the absolute accuracy between more than two properties. The well-established statistical technique of regression analysis is more pertinent to determining the accuracy of points derived from one property and any number of other properties. There are many instances in which relationships of this sort enable properties to be predicted from other measured properties with as good precision as they can be measured by a single test. It would be possible to examine in this way the relationships between all the specified properties of a product and to establish certain key properties from which the remainder could be predicted, but this would be a tedious task.

An alternative approach to that of picking out the essential tests in a specification using regression analysis is to take a look at the specification as a whole and extract the essential features (termed *principal components analysis*).

Principal components analysis (see also p. 16) involves an examination of set of data as points in *n*-dimensional space (corresponding to *n* original tests) and determines (first) the direction that accounts for the biggest variability in the data (*first principal component*). The process is repeated until *n* principal components are evaluated, but not all of these are of practical importance because some may be attributable purely to experimental error. The number of significant principal components shows the number of independent properties being measured by the tests considered.

Following from this, it is necessary to establish the number of independent properties that are necessary to predict product performance in service with the goals of rendering any specification more meaningful and allowing a high degree of predictability of product behavior. For a long-term approach it might be possible to obtain new tests of a fundamental nature to replace, or certainly to supplement, existing tests. In the short term, selecting the best of the existing tests to define product quality is the most beneficial route to predictability.

1.9. PRECISION

The *precision* of a test method is the variability between test results obtained on the same material using the specific test method. The precision of a test is usually unrelated to its accuracy. The results may be precise but not necessarily accurate. In fact, the precision of an analytical method is the amount of scatter in the results obtained from multiple analyses of a homogeneous sample. To be meaningful, the precision study must be performed using the exact sample and standard preparation procedures that will be used in the final method. *Precision* is expressed as *repeatability* and *reproducibility*.

The *intralaboratory precision* or *within-laboratory precision* refers to the precision of a test method when the results are obtained by the same operator in the same laboratory using the same apparatus. In some cases, the precision is applied to data gathered by a different operator in the same laboratory using the same apparatus. Thus intralaboratory precision has an expanded meaning insofar as it can be applied to laboratory precision.

Repeatability or *repeatability interval* of a test (*r)* is the maximum permissible difference due to test error between two results obtained on the same material in the same laboratory.

$$r = 2.77 \times \text{standard deviation of test}$$

The repeatability interval *r* is, statistically, the 95% probability level, that is, the differences between two test results are unlikely to exceed this repeatability interval more than five times in a hundred.

The *interlaboratory precision* or *between-laboratory precision* is defined in terms of the variability between test results obtained on the aliquots of the same homogeneous material in different laboratories using the same test method.

The term *reproducibility* or *reproducibility interval* (*R*) is analogous to the term repeatability, but it is the maximum permissible difference between two results obtained on the same material but now in different laboratories. Therefore, differences between two or more laboratories should not exceed the reproducibility interval more than five times in a hundred.

$$R = 2.77 \times \text{standard deviation of test}$$

The repeatability value and the reproducibility value have important implications for quality. As the demand for clear product specifications, and hence control over product consistency grows, it is meaningless to establish product specifications that are more restrictive than the reproducibility/repeatability values of the specification test methods.

1.10. METHOD VALIDATION

Method validation is the process of proving that an analytical method is acceptable for its intended purpose. Many organizations, such as the ASTM, provide a framework for performing such validations. In general, methods for product specifications and regulatory submission must include studies on specificity, linearity, accuracy, precision, range, detection limit, and quantitation limit.

The process of method development and validation covers all aspects of the analytical procedure, and the best way to minimize method problems is to perform validation experiments during development.

In performing validation studies, the approach should be viewed with the understanding that validation requirements are continually changing and vary widely depending on the type of product under tested and compliance with any necessary regulatory group.

In the early stages of new product development, it may not be necessary to perform all of the various validation studies. However, the process of validating a method cannot be separated from the actual development of the method conditions, because the developer will not know whether the method conditions are acceptable until validation studies are performed. The development and validation of a new analytical method may therefore be an iterative process. Results of validation studies may indicate that a change in the procedure is necessary, which may then require revalidation. During each validation study, key method parameters are determined and then used for all subsequent validation steps.

The first step in the method development and validation cycle should be to set minimum requirements, which are essentially acceptance specifications for the method. A complete list of criteria should be agreed on during method development with the end users before the method is developed so that expectations are clear. Once the validation studies are complete, the method developers should be confident in the ability of the method to provide good quantitation in their own laboratories. The remaining studies should provide greater assurance that the method will work well in other laboratories, where different operators, instruments, and reagents are involved and where it will be used over much longer periods of time.

The remaining precision studies comprise much of what is often referred to as *ruggedness*. *Intermediate precision* is the precision obtained when an assay is performed by multiple analysts using several instruments on different days in one laboratory. Intermediate precision results are used to identify which of the above factors contribute significant variability to the final result.

The last type of precision study is *reproducibility* (*q.v.*), which is determined by testing homogeneous samples in multiple laboratories, often as part of interlaboratory crossover studies. The evaluation of reproducibility results often focuses more on measuring bias in results than on determining differences in precision alone. Statistical equivalence is often used as a measure of acceptable interlaboratory results. An alternative, more practical approach is the use of *analytical equivalence*, in which a range of acceptable results is chosen before the study and used to judge the acceptability of the results obtained from the different laboratories.

Performing a thorough method validation can be a tedious process, but the quality of data generated with the method is directly linked to the quality of this process. Time constraints often do not allow for sufficient method validation. Many researchers have experienced the consequences of invalid methods and realized that the amount of time and resources required to solve problems discovered later exceeds what would have been expended initially if the validation studies had been performed properly. *Putting in time and effort up front* will help any analyst to find a way through the method validation maze and will eliminate many of the problems common to inadequately validated analytical methods.

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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 constituents 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 2.1. Classification by Chemical Composition (adapted from Speight, 1999)

Composition of 250–300°C (480–570°F) Fraction					Crude oil Classification
Paraffinic %	Naphthenic %	Aromatic %	Wax %	Asphalt %	
>46, <61	>22, <32	>12, <25	<10	<6	Paraffinic
>42, <45	>38, <39	>16, <20	<6	<6	Paraffinic-naphthenic
>15, <26	>61, <76	>8, <13	0	<6	Naphthenic
>27, <35	>36, <47	>26, <33	<1	<10	Paraffinic-naphthenic-aromatic
<8	>57, <78	>20, <25	<0.5	<20	Aromatic

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 (°K = °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,

$$\mathrm{CI} = 473.7d - 456.8 + 48{,}640/K$$

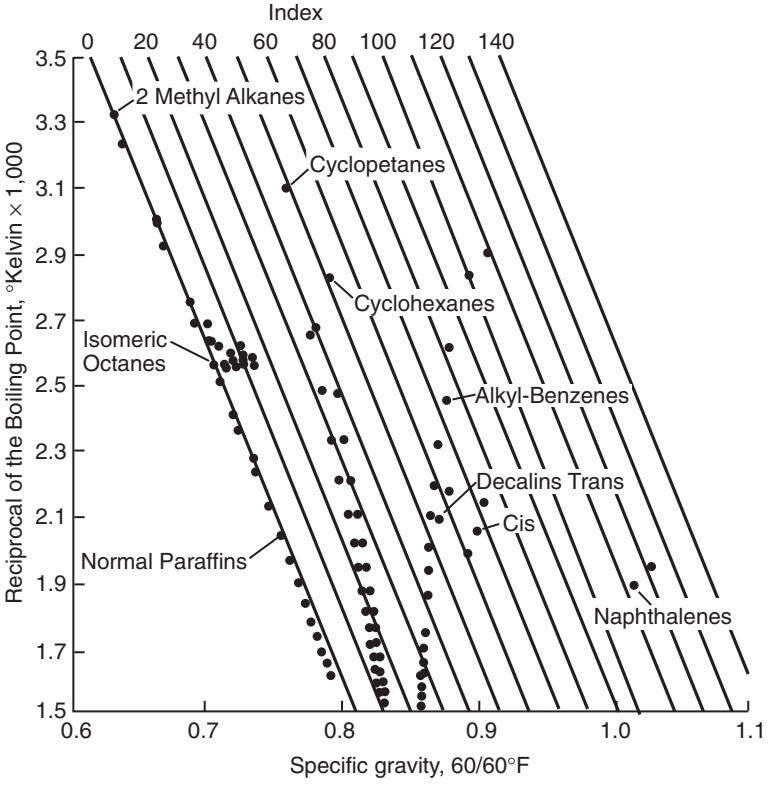

Figure 2.1. Reference data for the correlation index (from Speight, 1999)

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:

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

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

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

* 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:

$$\text{API gravity (degrees)} = (141.5/\text{sp gr } 60/60°\text{F}) - 131.5$$

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: l5.5–149°C (60–300°F)
3. Kerosene (medium naphtha), boiling range: 149–232°C (300–450°F)
4. Gas oil, boiling range: 232–343°C (450–650°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-l160, 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:

$$2NaCl + H_2O \rightarrow 2\ HCl + Na_2O$$

$$MgCl_2 + H_2O \rightarrow 2\ HCl + MgO$$

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 nonaqueous 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 (H_2SO_4) by means of hydrogen peroxide (H_2O_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 (NaOH) solution. Alternatively, the sample can be burned in air and the sulfur as sulfate in the absorbent determined gravimetrically as barium sulfate ($BaSO_4$) 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 Kα line at 5.373Å is measured. The background intensity, measured at 5.190Å, 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 avaibale 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°C (–288°F) to temperatures in excess of 1100°C (2000°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*,

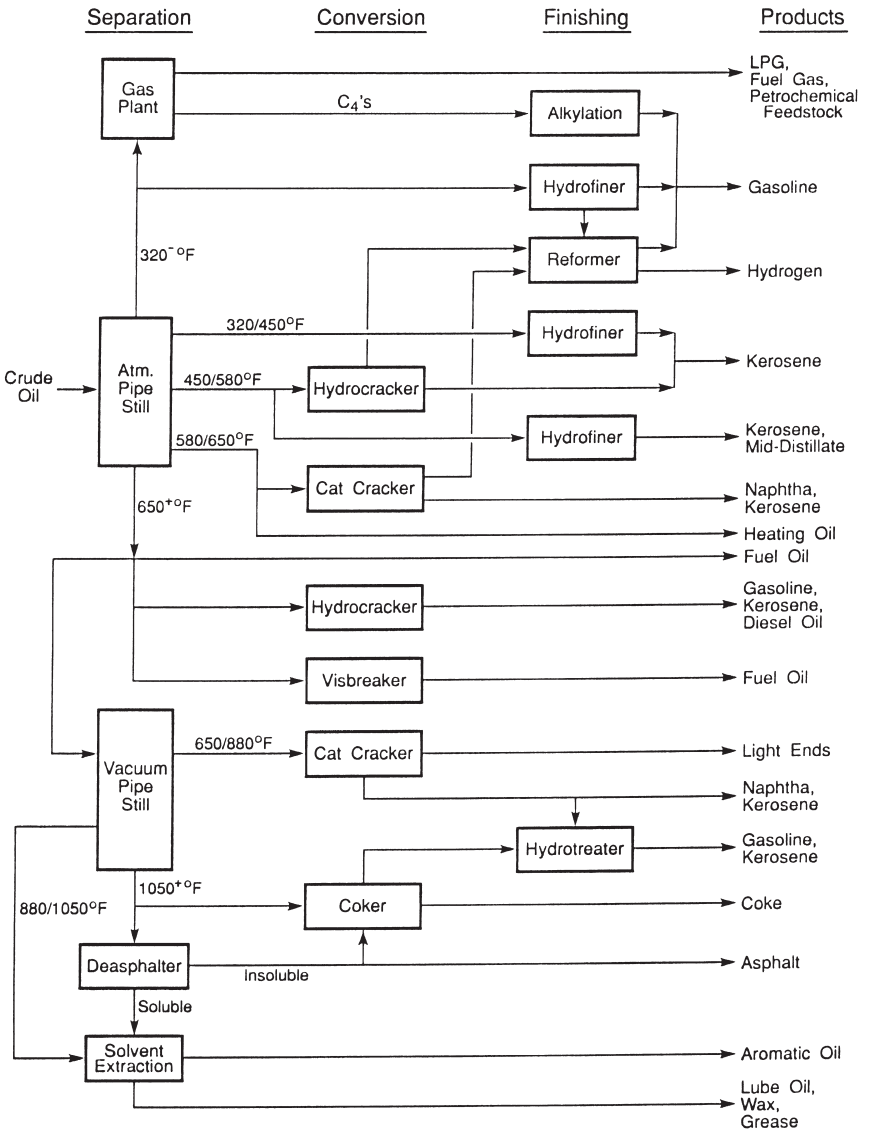

Figure 2.2. Schematic of a petroleum refinery (from Speight, 1999)

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

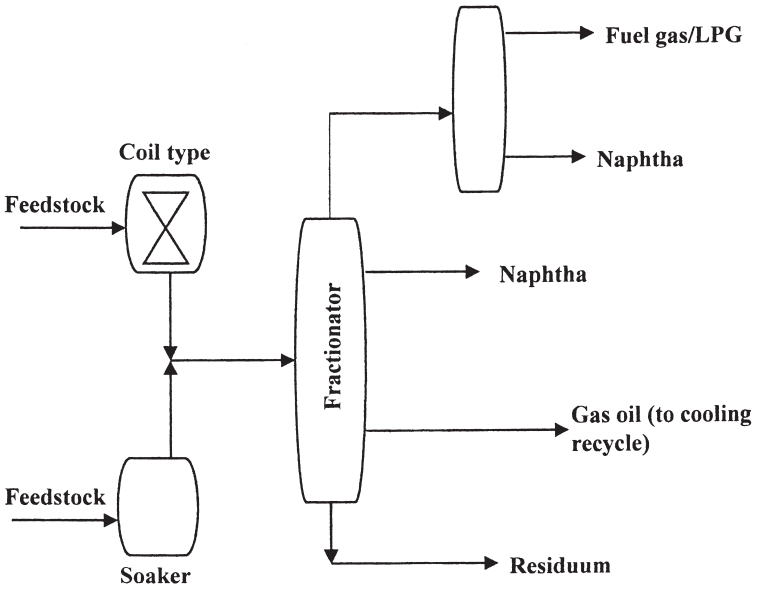

Figure 2.3. The visbreaking process

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

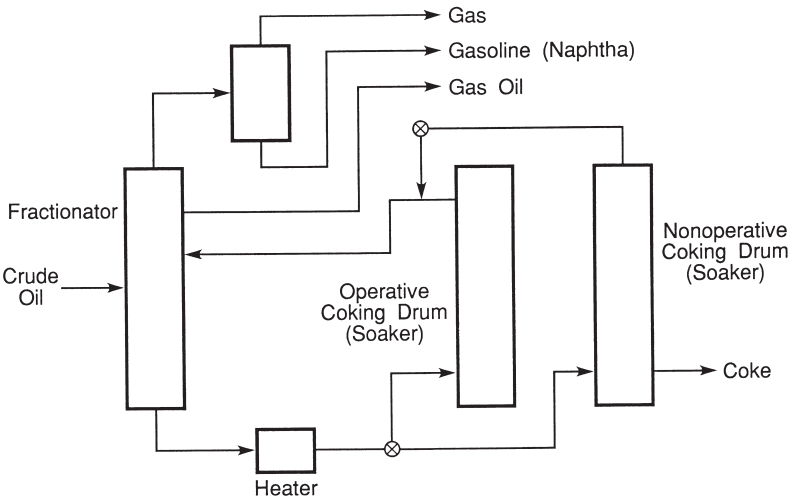

Figure 2.4. The delayed coking process

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

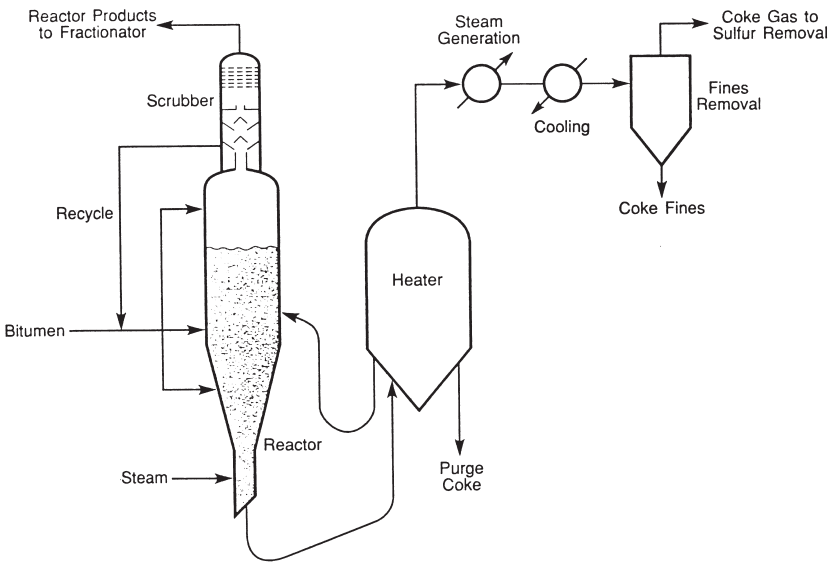

Figure 2.5. The fluid coking process

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/ft^3. 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-

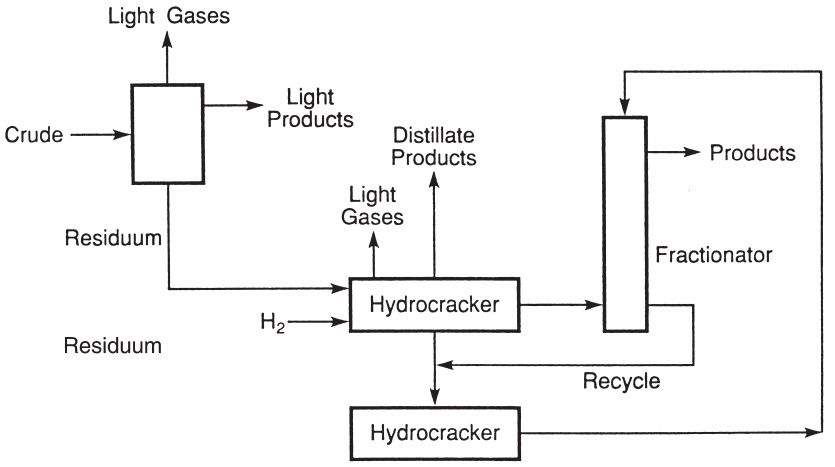

Figure 2.6. The hydrocracking process

atomic species (nitrogen, oxygen, and sulfur) as the respective hydrogenated analogs (ammonia, NH_3, water, H_2O, and hydrogen sulfide, H_2S). 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.

Table 2.3. Composition of Associated Natural Gas From a Petroleum Well (adapted from Speight, 1999)

Category	Component	Amount (%)
Paraffinic	Methane (CH_4)	70–98
	Ethane (C_2H_6)	1–10
	Propane (C_3H_8)	Trace–5
	Butane (C_4H_{10})	Trace–2
	Pentane (C_5H_{12})	Trace–1
	Hexane (C_6H_{14})	Trace–0.5
	Heptane and higher (C_7^+)	None–trace
Cyclic	Cyclopropane (C_3H_6)	Traces
	Cyclohexane (C_6H_{12})	Traces
Aromatic	Benzene (C_6H_6), others	Traces
Non-hydrocarbon	Nitrogen (N_2)	Trace–15
	Carbon dioxide (CO_2)	Trace–1
	Hydrogen sulfide (H_2S)	Trace occasionally
	Helium (He)	Trace–5
	Other sulfur and nitrogen compounds	Trace occasionally
	Water (H_2O)	Trace–5

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 ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$), *iso*-butane [$CH_3CH(CH_3)CH_3$] and to a lesser extent propylene ($CH_3CH{:}CH_2$), or butylene ($CH_3CH_2CH{:}CH_2$). 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 (CH_4). Other constituents are paraffinic hydrocarbons such as ethane (CH_3CH_3), propane, and the butanes. Many natural gases contain nitrogen (N_2) as well as carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Trace quantities of argon, hydro-

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

	Composition (vol%)		
Constituents	Wet	Range	Dry
Hydrocarbons			
Methane	84.6		96.0
Ethane	6.4		2.0
Propane	5.3		0.6
Isobutane	1.2		0.18
n-Butane	1.4		0.12
Isopentane	0.4		0.14
n-Pentane	0.2		0.06
Hexanes	0.4		0.10
Heptanes	0.1		0.80
Non-hydrocarbons			
Carbon dioxide		0–5	
Helium		0–0.5	
Hydrogen sulfide		0–5	
Nitrogen		0–10	
Argon		0–0.05	
Radon, krypton, xenon		Traces	

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-

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/ft^3), 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 nonhydrocarbon 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

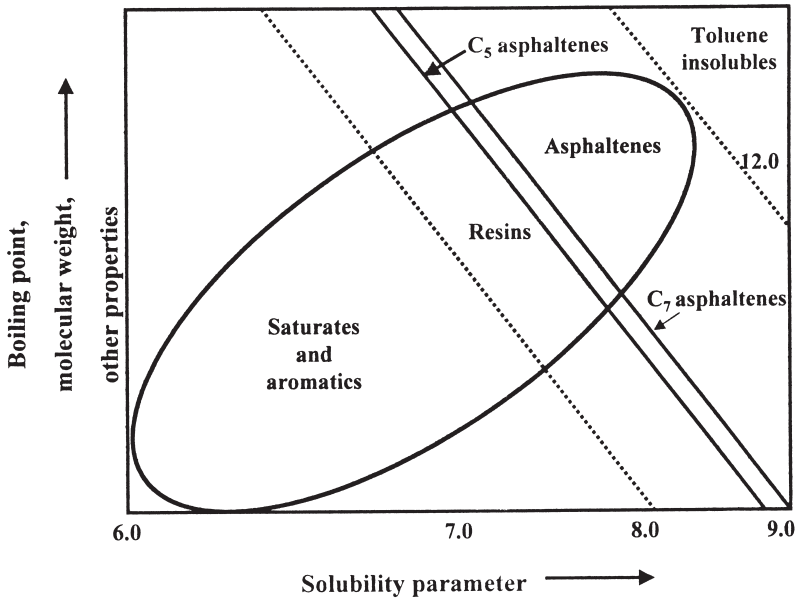

Figure 2.7. Map for fractional separation of petroleum

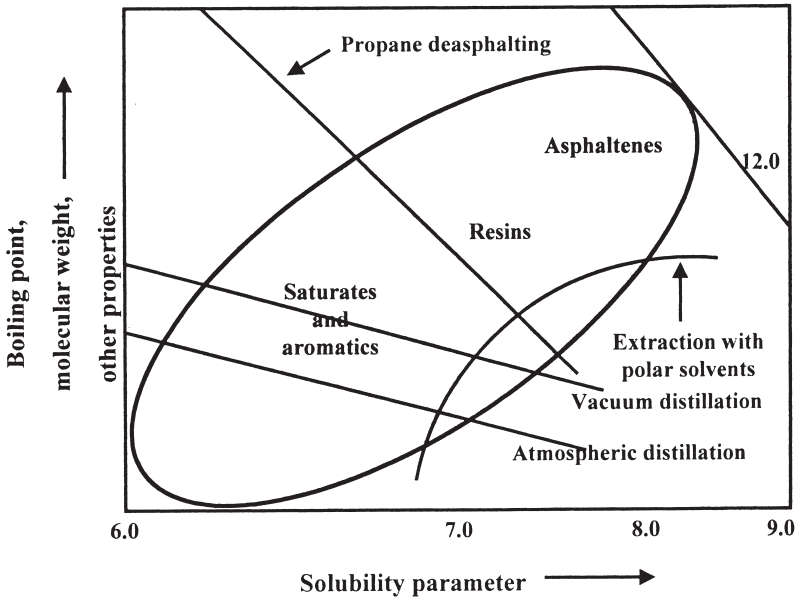

Figure 2.8. Separation processes from a petroleum map

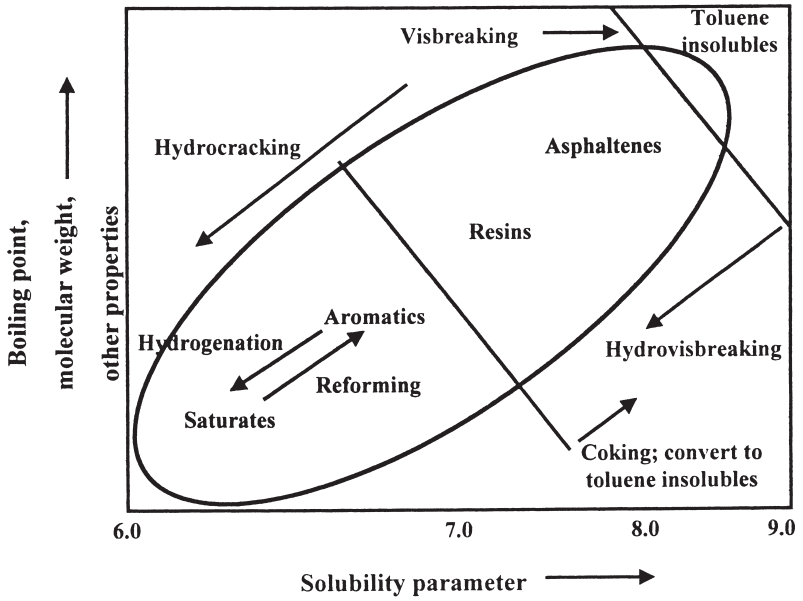

Figure 2.9. Conversion processes from a petroleum map

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.

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CHAPTER

3

GASES

3.1. INTRODUCTION

The terms *petroleum gas* and *refinery gas* are often used to identify liquefied petroleum gas (LPG) or even gas that emanates from the top of a refinery distillation column. For the purpose of this text, "petroleum gas" not only describes liquefied petroleum gas but also natural gas and refinery gas (Guthrie, 1967; Francis and Peters, 1980; Rawlinson and Ward, 1973; Hoffman, 1983; Moustafa, 1996; Speight, 1999). In this chapter, each gas is, in turn, referenced by its name rather than the generic term *petroleum gas* (ASTM D-4150). However, the composition of each gas varies (Table 3.1) and recognition of this is essential before testing protocols are applied.

The first and most important aspect of gaseous testing is the measurement of the volume of gas (ASTM D-1071). In this test method, several techniques are described and may be employed for any purpose where it is necessary to know the quantity of gaseous fuel. In addition, the thermophysical properties of methane (ASTM D-3956), ethane (ASTM D-3984), propane (ASTM D-4362), *n*-butane (ASTM D-4650), and *iso*-butane (ASTM D-4651) should be available for use and consultation (see also Stephenson and Malanowski, 1987).

3.1.1. Liquefied Petroleum Gas

Liquefied petroleum gas (LPG) is a mixture of the gaseous hydrocarbons propane ($CH_3CH_2CH_3$, boiling point: –42°C, –44°F) and butane ($CH_3CH_2CH_2CH_3$, boiling point: 0°C, 32°F) that are produced during natural gas refining, petroleum stabilization, and petroleum refining (Austin, 1984; Speight, 1999; Ritter, 2000). The propane and butane can be derived from natural gas or from refinery operations, but in the latter case substantial proportions of the corresponding olefins will be present and must be separated. The hydrocarbons are normally liquefied under pressure for transportation and storage.

The presence of propylene and butylenes in liquefied petroleum gas used as fuel gas is not critical. The vapor pressures of these olefins are slightly higher than those of propane and butane and the flame speed is

Table 3.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

substantially higher, but this may be an advantage because the flame speeds of propane and butane are slow. However, one issue that often limits the amount of olefins in liquefied petroleum gas is the propensity of the olefins to form soot.

In addition, liquefied petroleum gas is usually available in different grades (usually specified as Commercial Propane, Commercial Butane, Commercial Propane-Butane (P-B) Mixtures, and Special Duty Propane) (Rawlinson and Ward, 1973). During the use of liquefied petroleum gas, the gas must vaporize completely and burn satisfactorily in the appliance without causing any corrosion or producing any deposits in the system.

Commercial Propane consists predominantly of propane and/or propylene, whereas *Commercial Butane* is mainly composed of butanes and/or butylenes. Both must be free from harmful amounts of toxic constituents and free from mechanically entrained water (which may be further limited by specifications) (ASTM D-1835). Analysis by gas chromatography is possible (IP 405).

Commercial Propane-Butane mixtures are produced to meet particular requirements such as volatility, vapor pressure, specific gravity, hydrocarbon composition, sulfur and its compounds, corrosion of copper, residues, and water content. These mixtures are used as fuels in areas and at times where low ambient temperatures are less frequently encountered. Analysis by gas chromatography is possible (ASTM D-5504, ASTM D-6228, IP 405).

Special Duty Propane is intended for use in spark-ignition engines, and the specification includes a minimum *motor octane number* to ensure

satisfactory antiknock performance. Propylene ($CH_3CH=CH_2$) has a significantly lower octane number (ASTM D-2623) than propane, so there is a limit to the amount of this component that can be tolerated in the mixture. Analysis by gas chromatography is possible (ASTM D-5504, ASTM D-6228, IP 405).

Liquefied petroleum gas and liquefied natural gas can share the facility of being stored and transported as a liquid and then vaporized and used as a gas. To achieve this, liquefied petroleum gas must be maintained at a moderate pressure but at ambient temperature. The liquefied natural gas can be at ambient pressure but must be maintained at a temperature of roughly –1 to 60°C (30–140°F). In fact, in some applications it is actually economical and convenient to use liquefied petroleum gas in the liquid phase. In such cases, certain aspects of gas composition (or quality such as the ratio of propane to butane and the presence of traces of heavier hydrocarbons, water, and other extraneous materials) may be of lesser importance compared with the use of the gas in the vapor phase.

For normal (gaseous) use, the contaminants of liquefied petroleum gas are controlled at a level at which they do not corrode fittings and appliances or impede the flow of the gas. For example, hydrogen sulfide (H_2S) and carbonyl sulfide (COS) should be absent. Organic sulfur to the level required for adequate odorization (ASTM D-5305), or *stenching*, is a normal requirement in liquefied petroleum gas; dimethyl sulfide (CH_3SCH_3) and ethyl mercaptan (C_2H_5SH) are commonly used at a concentration of up to 50 ppm. Natural gas is similarly treated, possibly with a wider range of volatile sulfur compounds.

The presence of water in liquefied petroleum gas (or in natural gas) is undesirable because it can produce hydrates that will cause, for example, line blockage due to the formation of hydrates under conditions where the water *dew point* is attained (ASTM D-1142). If the amount of water is above acceptable levels, the addition of a small amount of methanol will counteract any such effect.

In addition to other gases, liquefied petroleum gas may also be contaminated by higher-boiling constituents such as the constituents of middle distillates to lubricating oil. These contaminants become included in the gas during handling and must be prevented from reaching unacceptable levels. Olefins and especially diolefins are prone to polymerization and should be removed.

3.1.2. Natural Gas

Natural gas is found in petroleum reservoirs as free gas (*associated gas*), in solution with petroleum in the reservoir (*dissolved gas*), or in reservoirs that contain only gaseous constituents and no (or little) petroleum

(*unassociated gas*) (Austin, 1984; Speight, 1999; Cranmore and Stanton, 2000). The hydrocarbon content varies from mixtures of methane and ethane with very few other constituents (*dry* gas) to mixtures containing all of the hydrocarbons from methane to pentane and even hexane (C_6H_{14}) and heptane (C_7H_{16}) (*wet* gas). In both cases, some carbon dioxide (CO_2) and inert gases, including helium (He), are present together with hydrogen sulfide (H_2S) and a small quantity of organic sulfur.

Although the major subject of this chapter is liquefied petroleum gas, the term "petroleum gas(es)" in this context is also used to describe the gaseous phase and liquid phase mixtures comprised mainly of methane to butane (C_1 to C_4 hydrocarbons) that are dissolved in the crude oil and natural gas, as well as gases produced during thermal processes in which the crude oil is converted to other products. It is necessary, however, to acknowledge that in addition to the hydrocarbons, gases such as carbon dioxide, hydrogen sulfide, and ammonia are also produced during petroleum refining and will be constituents of refinery gas that must be removed. Olefins are also present in the gas streams of various processes and are not included in liquefied petroleum gas but are removed for use in petrochemical operations (Crawford et al., 1993).

Raw natural gas varies greatly in composition (Table 3.2), and the constituents can be several of a group of hydrocarbons (Table 3.3) and non-hydrocarbons. The treatment required to prepare natural gas for

Table 3.2. Composition of Associated Natural Gas From a Petroleum Well (adapted from Speight, 1999)

Category	Component	Amount (%)
Paraffinic	Methane (CH_4)	70–98
	Ethane (C_2H_6)	1–10
	Propane (C_3H_8)	Trace–5
	Butane (C_4H_{10})	Trace–2
	Pentane (C_5H_{12})	Trace–1
	Hexane (C_6H_{14})	Trace–0.5
	Heptane and higher (C_7^+)	None–trace
Cyclic	Cyclopropane (C_3H_6)	Traces
	Cyclohexane (C_6H_{12})	Traces
Aromatic	Benzene (C_6H_6), others	Traces
Non-hydrocarbon	Nitrogen (N_2)	Trace–15
	Carbon dioxide (CO_2)	Trace–1
	Hydrogen sulfide (H_2S)	Trace occasionally
	Helium (He)	Trace–5
	Other sulfur and nitrogen compounds	Trace occasionally
	Water (H_2O)	Trace–5

Table 3.3. Possible Constituents of Natural Gas and Refinery Gas

Gas	Molecular Weight	Boiling Point 1 atm °C (°F)	Density at 60°F (15.6°C), 1 atm	
			g/liter	Relative to Air = 1
Methane	16.043	–161.5 (–258.7)	0.6786	0.5547
Ethylene	28.054	–103.7 (–154.7)	1.1949	0.9768
Ethane	30.068	–88.6 (–127.5)	1.2795	1.0460
Propylene	42.081	–47.7 (–53.9)	1.8052	1.4757
Propane	44.097	–42.1 (–43.8)	1.8917	1.5464
1,2-Butadiene	54.088	10.9 (51.6)	2.3451	1.9172
1,3-Butadiene	54.088	–4.4 (24.1)	2.3491	1.9203
1-Butene	56.108	–6.3 (20.7)	2.4442	1.9981
cis-2-Butene	56.108	3.7 (38.7)	2.4543	2.0063
trans-2-Butene	56.108	0.9 (33.6)	2.4543	2.0063
iso-Butene	56.104	–6.9 (19.6)	2.4442	1.9981
n-Butane	58.124	–0.5 (31.1)	2.5320	2.0698
iso-Butane	58.124	–11.7 (10.9)	2.5268	2.0656

distribution as a industrial or household fuel is specified in terms of the use and environmental regulations. .

Carbon dioxide (ASTM D-1137, ASTM D-1945, ASTM D-4984) in excess of 3% is normally removed for reasons of corrosion prevention (ASTM D-1838). Hydrogen sulfide (ASTM D-2420, ASTM D-2385, ASTM D-2725, ASTM D-4084, ASTM D-4810, IP 103, IP 272) is also removed, and the odor of the gases must not be objectionable (ASTM D-6273) so mercaptan content (ASTM D-1988, ASTM D-2385, IP 272) is important. A simple lead acetate test (ASTM D-2420, ASTM D-4084) is available for detecting the presence of hydrogen sulfide and is an additional safeguard that hydrogen sulfide not be present (ASTM D-1835). Methyl mercaptan, if present, produces a transitory yellow stain on the lead acetate paper that fades completely in less than 5 min. Other sulfur compounds (ASTM D-5504, ASTM D-6228) present in liquefied petroleum gas do not interfere.

In the lead acetate test (ASTM D-2420), the vaporized gas is passed over moist lead acetate paper under controlled conditions. Hydrogen sulfide reacts with lead acetate to form lead sulfide, resulting in a stain on the paper varying in color from yellow to black depending on the amount of hydrogen sulfide present. Other pollutants can be determined by gas chromatography (ASTM D-5504, ASTM D-6228, IP 318).

The total sulfur content (ASTM D-1072, ASTM D-2784, ASTM D-3031) is normally acceptably low and frequently so low that it needs augmenting by means of alkyl sulfides, mercaptans, or thiophenes to maintain an acceptable safe level of odor.

The hydrocarbon dew point is reduced to such a level that retrograde condensation, that is, condensation resulting from pressure drop, cannot occur under the worst conditions likely to be experienced in the gas transmission system. Similarly, the water dew point is reduced to a level sufficient to preclude formation of C_1 to C_4 hydrates in the system.

The natural gas after appropriate treatment for acid gas reduction, odorization, and hydrocarbon and moisture dew point adjustment (ASTM D-1142) would then be sold within prescribed limits of pressure, calorific value, and possibly Wobbe index [cv/(sp. gr.)].

3.1.3. Refinery Gas

Refinery gas is the noncondensable gas that is obtained during distillation or treatment (cracking, thermal decomposition) of petroleum (Austin, 1984; Speight, 1999; Robinson and Faulkner, 2000). It consists mainly of hydrogen (H_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and olefins ($RCH{=}CHR^1$, where R and R^1 can be hydrogen or a methyl group) and may also include off-gases from petrochemical processes (Table 3-3). Olefins such as ethylene (ethene, $CH_2{=}CH_2$, boiling point: –104°C, –155°F), propene (propylene, $CH_3CH{=}CH_2$, boiling point: –47°C, –53°F), butene (butene-1, $CH_3CH_2CH{=}CH_2$, boiling point: –5°C, 23°F) *iso*-butylene [$(CH_3)_2C{=}CH_2$, boiling point –6°C, 21°F], *cis*- and *trans*-butene-2 ($CH_3CH{=}CHCH_3$, boiling point: ~1°C, 30°F), and butadiene ($CH_2{=}CHCH{=}CH_2$, boiling point: –4°C, 24°F) as well as higher-boiling olefins are produced by various refining processes.

In all cases, it is the composition of the gas in terms of *hydrocarbon type* that is more important in the context of the application. For example, in petrochemical applications, the presence of propylene and butylene above 10% v/v can have an adverse effect on hydrodesulfurization before steam reforming. On the other hand, petrochemical processes, such as in the production of *iso*-octane from *iso*-butane and butylene, can require the exclusion of the saturated hydrocarbons.

Refinery gas specifications will vary according to the gas quality available and the end use (Rawlinson and Ward, 1973; Johansen, 1998). For fuel uses, gas as specified above presents little difficulty when used as supplied. Alternatively, a gas of constant Wobbe index, say for gas turbine use, could readily be produced by the user. Part of the combustion air would be diverted into the gas stream by a Wobbe index controller. This would be set to supply gas at the lowest Wobbe index of the undiluted gas.

Residual refinery gases, usually in more than one stream, which allows a degree of quality control, are treated for hydrogen sulfide removal, and gas sales are usually on a thermal content (calorific value, heating value) basis with some adjustment for variation in the calorific value and hydrocarbon type (Rawlinson and Ward, 1973; McKetta, 1993; Speight, 1993; Cranmore and Stanton, 2000).

3.2. SAMPLING

One of the more critical aspects for the analysis of low-boiling hydrocarbons is the question of volumetric measurement (ASTM D-1071) and sampling (ASTM D-1145, ASTM D-1247, ASTM D-1265). However, sampling liquefied petroleum gas from a liquid storage system is complicated by existence of two phases (gas and liquid), and the composition of the supernatant vapor phase will, most probably, differ from the composition of the liquid phase. Furthermore, the compositions of both phases will vary as a sample (or sample) is removed from one or both phases. An accurate check of composition can only be made if samples are taken during filling of the tank or from a fully charged tank.

In general, the sampling of gaseous constituents and of liquefied gases is the subject of a variety of sampling methods (ASTM D-5503), such as the manual method (ASTM D-1265, ASTM D-4057), the floating piston cylinder method (ASTM D-3700), and the automatic sampling method (ASTM D-4177, ASTM D-5287). Methods for the preparation of gaseous and liquid blends are also available (ASTM D-4051, ASTM D-4307), including the sampling and handling of fuels for volatility measurements (ASTM D-5842).

Sampling methane (CH_4) and ethane (C_2H_6) hydrocarbons is usually achieved using stainless steel cylinders, either lined or unlined. However, other containers may also be used depending on particular situations. For example, glass cylinder containers or polyvinyl fluoride (PVF) sampling bags may also be used but, obviously, cannot be subjected to pressures that are far in excess of ambient pressure. The preferred method for sampling propane (C_3H_8) and butane (C_4H_{10}) hydrocarbons is by the use of piston cylinders (ASTM D-3700), although sampling these materials as gases is also acceptable in many cases. The sampling of propane and higher-boiling hydrocarbons is dependent upon the vapor pressure of the sample (IP 410). Piston cylinders or pressurized steel cylinders are recommended for high-vapor-pressure sampling where significant amounts of low-boiling gases are present, whereas atmospheric sampling may be used for samples having a low vapor pressure.

3.3. PROPERTIES AND TEST METHODS

Hydrocarbon gases are amenable to analytical techniques, and there has been the tendency (and it remains) for the determination of both major constituents and trace constituents more than is the case with the heavier hydrocarbons. The complexity of the mixtures that are evident as the boiling point of petroleum fractions and petroleum products increases makes identification of many of the individual constituents difficult, if not impossible. In addition, methods have been developed for the determination of physical characteristics such as calorific value, specific gravity, and enthalpy from the analyses of mixed hydrocarbon gases, but the accuracy does suffer when compared with the data produced by methods for the direct determination of these properties.

Bulk physical property tests, such as density and heating value, as well as some compositional tests, such as the Orsat analysis and the mercuric nitrate method for the determination of unsaturation, are still used.

However, the choice of a particular test rests on the decision of the analyst that, in turn, depends on the nature of the gas under study. For example, judgment by the analyst is necessary as to whether or not a test that is applied to liquefied petroleum gas is suitable for natural gas insofar as inference from the non-hydrocarbon constituents will be minimal.

3.3.1. Calorific Value (Heat of Combustion)

Satisfactory combustion of hydrocarbon gases depends on the matching of burner and appliance design with certain gas characteristics. Various types of test methods are available for the direct determination of calorific value (ASTM D-900, ASTM D-1826, ASTM D-3588, ASTM D-4981).

The most important of these are the Wobbe index [WI; or Wobbe number = calorific value/(specific gravity] and the flame speed, usually expressed as a factor or an arbitrary scale on which the value of hydrogen is 100. This factor can be calculated from the gas analysis. In fact, calorific value and specific gravity can be calculated from compositional analysis (ASTM D-3588).

The Wobbe number gives a measure of the heat input to an appliance through a given aperture at a given gas pressure. By using this as a vertical coordinate and the flame speed factor (fsf) as the horizontal coordinate a combustion diagram can be constructed for an appliance, or a whole range of appliances, with the aid of appropriate test gases. This diagram shows the area within which variations in the WI and fsf of gases may occur for the given range of appliances without resulting in incomplete combustion, flame lift, or the lighting back of preaerated flames. This method of prediction of combustion characteristics is not sufficiently accurate to eliminate entirely the need for the practical testing of new gases.

Another important combustion criterion is the gas modulus, M = P/W, where P is the gas pressure and W is the Wobbe number of the gas. This must remain constant if a given degree of aeration is to be maintained in a preaerated burner using air at atmospheric pressure.

3.3.2. Composition

Liquefied petroleum gas, natural gas, and refinery gas are mixtures of products or naturally occurring materials and, fortunately, are relatively simple mixtures that do not suffer the complexities of the isomeric variations of the higher-molecular-weight hydrocarbons (Table 3.4; Drews, 1998).

Thus, because of the lower-molecular-weight constituents of these gases and their volatility, gas chromatography has been the technique of choice for fixed gas and hydrocarbon speciation and mass spectrometry is also a method of choice for compositional analysis of low-molecular-weight hydrocarbons (ASTM D-2421, ASTM D-2650). More recently, piggyback methods (such as gas chromatography/mass spectrometry and other double-technique methods) have been developed for the identification of gaseous and low-boiling liquid constituents of mixtures. The hydrocarbon composition is limited as to the total amount of ethane, butane, or pentane as well as ethylene and total dienes.

By limiting the amount of hydrocarbons that are lower boiling than the main component, the vapor pressure control is reinforced. Tests are avail-

Table 3.4. Number of Isomers for Selected Hydrocarbons

Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

able for vapor pressure at 100°F (38°C) (ASTM D-1267) and at 113°F (45°C) (IP 161). The limitation on the amount of higher-boiling hydrocarbons supports the volatility clause. The vapor pressure and volatility specifications will often be met automatically if the hydrocarbon composition is correct.

The amount of ethylene is limited because it is necessary to restrict the amount of unsaturated components so as to avoid the formation of deposits caused by the polymerization of the olefin(s). In addition, ethylene (boiling point: –104°C, –155°F) is more volatile than ethane (boiling point: –88°C, –127°F), and therefore a product with a substantial proportion of ethylene will have a higher vapor pressure and volatility than one that is predominantly ethane. Butadiene is also undesirable because it may also produce polymeric products that form deposits and cause blockage of lines.

Currently the preferred method for the analysis of liquefied petroleum gas, and indeed for most petroleum-related gases, is gas chromatography (ASTM D-2163, IP 264). This technique can be used for the identification and measurement of both main constituents and trace constituents. However, there may be some accuracy issues that arise in the measurement of the higher-boiling constituents because of relative volatility under the conditions in which the sample is held.

Capillary column gas chromatography is an even quicker and equally accurate alternative. Mass spectrometry (ASTM D-1137) is also suitable for analysis of petroleum gases. Of the other spectroscopic techniques, infrared and ultraviolet absorption may be applied to petroleum gas analysis for some specialized applications. Gas chromatography has also largely supplanted chemical absorption methods of analysis, but again these may have some limited specialized application.

Once the composition of a mixture has been determined it is possible to calculate various properties such as specific gravity, vapor pressure, calorific value and dew point.

Simple evaporation tests in conjunction with vapor pressure measurement give a further guide to composition. In these tests a liquefied petroleum gas sample is allowed to evaporate naturally from an open graduated vessel. Results are recorded on the basis of volume/temperature changes, such as the temperature recorded when 95% has evaporated or the volume left at a particular temperature (ASTM D-1837).

Because dew point can be calculated from composition, direct determination of dew point for a particular liquefied petroleum gas sample is a measure of composition. It is, of course, of more direct practical value and if there are small quantities of higher-molecular-weight material present, it is preferable to use a direct measurement.

Specific gravity again can be calculated, but if it is necessary to measure it several pieces of apparatus are available. For determining the density or

specific gravity of liquefied petroleum gas in its liquid state there are two methods using a metal pressure pycnometer. A pressure hydrometer may be used (ASTM D-1267) for the relative density that may also be calculated from composition al analysis (ASTM D-2598). Various procedures, manual and recording, for specific gravity or density in the gaseous state are given in two methods (ASTM D-l070, IP 59). Calculation of the density is also possible using any one of four models, depending on the composition of the gas (ASTM D-4784).

Gases such as ethane that are destined for use as petrochemical feedstocks must adhere to stringent composition controls that are dependent on the process. For example, moisture content (ASTM D-1142), oxygen content (ASTM D-1945), carbon dioxide content (ASTM D-1945), and sulfur content (ASTM D-1072) must be monitored because they all interfere with catalyst performance in petrochemical processes.

The hydrocarbon composition of natural gasoline (although not specifically a gas) for petrochemical use must undergo a compositional analysis (ASTM D-2427) and a test for total sulfur (ASTM D-1266, IP 107, IP 191).

The presence of any component substantially less volatile than the main constituents of the liquefied petroleum gas will give rise to unsatisfactory performance. It is difficult to set limits for the amount and nature of the "residue" that will make a product unsatisfactory. Obviously, small amounts of oily material can block regulators and valves. In liquid vaporizer feed systems even gasoline-type material could cause difficulty.

The residue (ASTM D-2158) is a measure of the concentration of contaminants boiling above 37.8°C (100°F) that may be present in the gas.

Determination of the residue by the end point index (EPI) endeavors to give a measure of the heavier hydrocarbons, but the relationship between EPI, hydrocarbon range, and performance is not established.

Other methods are available that measure residue more directly, and for particular applications it may be possible to relate the values obtained to the performance required and so to set satisfactory limits.

Analytical methods are available in standard form for determining volatile sulfur content and certain specific corrosive sulfur compounds that are likely to be present. Volatile sulfur determination is made by a combustion procedure (ASTM D-l26, IP 107) that uses a modification of the standard wick-fed lamp. Many laboratories use rapid combustion techniques with an oxy-hydrogen flame in a Wickbold or Martin-Floret burner (ASTM D-2784, IP 243).

This test method (ASTM D-2784, IP 243) is valid for sulfur levels of >1 μg/g of sulfur in liquefied petroleum gas, but the samples should not contain more than 100 μg/g of chlorine. In the test, the sample is burned in an oxy-hydrogen burner or in a lamp in a closed system in a carbon dioxide-oxygen atmosphere. The latter is not recommended for trace quantities of sulfur

because of the inordinately long combustion times needed. The sulfur oxides produced are absorbed and oxidized to sulfuric acid in a hydrogen peroxide solution. The sulfate ions are then determined by either titrating with barium perchlorate solution and a thorinmethylene blue mixed indicator or by precipitating as barium sulfate and measuring the turbidity of the precipitate with a photometer.

Trace hydrocarbons that may be regarded as contaminants may be determined by the gas chromatographic methods already discussed. Heavier hydrocarbons in small amounts may not be completely removed from the column. If accurate information is required about the nature and amount of heavy ends then temperature programming or a concentration procedure may be used.

Analytical methods for determining traces of various other impurities, such as chlorides (ASTM D-2384), are known to be in use. The presence of acetylenes in refinery gases, although unlikely, must still be considered. Acetylenes can be determined with a chemical test method, whereas carbonyls are determined by the classic hydroxylamine hydrochloride reaction (ASTM D-1089).

The determination of traces of higher-boiling hydrocarbons and oily matter involves use of a method for residue that involves a preliminary weathering. The residue after weathering is dissolved in a solvent, and the solution is applied to a filter paper. The presence of residue is indicated by the formation of an oil stain. The procedure is taken further by combining the oil stain observation with other observed values to calculate an end point index (ASTM D-2158). The method is not very precise, and work is proceeding in several laboratories to develop a better method for the determination of residue in the form of oily matter.

In liquefied petroleum gas where the composition is such that the hydrocarbon dew point is known to be low, a dew point method will detect the presence of traces of water (ASTM D-1142).

The odor of liquefied petroleum gas must be detectable to avoid the risk of explosion. Odor is a very subjective matter, and no standard method is available. It is desirable to set up some system in which the concentration of gas can be measured in relation to its explosive limits and in which some variables can be standardized, for example, flow rate and orifice size. This will ensure that in any one location the liquefied petroleum gas is always being assessed under similar conditions from day to day.

Propane, *iso*-butane (boiling point: –12°C, 11°F), and butane generally constitute this sample type and are used for heating and motor fuels and as chemical feedstocks (ASTM D-2597, ASTM D-2504, ASTM D-2505).

Procedures for the determination of hydrogen, helium, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethene, ethane, propane, butanes, pentanes, and hexanes-plus in natural and reformed gases by

packed column gas chromatography are available (ASTM D-1945, ASTM D-1946). These compositional analyses are used to calculate many other properties of gases, such as density, heating value, and compressibility. The first five components listed are determined with a molecular sieve column (argon carrier gas), whereas the remaining components are determined with polydimethylsiloxane partition or porous polymer columns. The hexanes-plus analysis is accomplished by backflushing the column after the elution of pentane or by the use of a backflushed precolumn.

Important constituents of natural gas not accounted for in these analyses are moisture (water) and hydrogen sulfide, as well as other sulfur compounds (ASTM D-1142, ASTM D-1988, ASTM D-5454, ASTM D-4888, ASTM D-5504, ASTM D-6228).

Olefins (ethylene, propylene, butylenes, and pentylenes) that occur in refinery (process) gas have specific characteristics and require specific testing protocols (ASTM D-5234, ASTM D-5273, ASTM D-5274).

Thus hydrocarbon analysis of ethylene is accomplished by two methods (ASTM D-2505, ASTM D-6159), one of which (ASTM D-6159) uses wide-bore (0.53 mm) capillary columns, including a Al_2O_3/KCl PLOT column. Another method (ASTM D-2504) is recommended for determination of noncondensable gases, and yet another (ASTM D-2505) is used for the determination of carbon dioxide.

Hydrocarbon impurities in propylene can be determined by gas chromatographic methods (ASTM D-2712, ASTM D-2163), and another test is available for determination of traces of methanol in propylene (ASTM Test Method D4864). A gas chromatographic method (ASTM D-5303) is available for the determination of trace amounts of carbonyl sulfide in propylene with a flame photometric detector. Also, sulfur in petroleum gas can be determined by oxidative microcoulometry (ASTM D-3246).

Commercial butylenes, high-purity butylenes, and butane-butylene mixtures are analyzed for hydrocarbon constituents (ASTM D-4424), and hydrocarbon impurities in 1,3-butadiene can also be determined by gas chromatography (ASTM D-2593). The presence of butadiene dimer and styrene is determined in butadiene by gas chromatography (ASTM D-2426).

Carbonyls in C_4 hydrocarbons are determined by a titrimetric technique (ASTM D-4423) and by use of a peroxide method (ASTM D-5799).

In general, gas chromatography will undoubtedly continue to be the method of choice for characterization of light hydrocarbon materials. New and improved detection devices and techniques, such as chemiluminescence, atomic emission, and mass spectroscopy, will enhance selectivity, detection limits, and analytical productivity. Laboratory automation through autosampling, computer control, and data handling will provide improved precision and productivity, as well as simplified method operation.

Compositional analysis can be used to calculate calorific value, specific gravity, and compressibility factor (ASTM D-3588).

Mercury in natural gas is also measured by atomic fluorescence spectroscopy (ASTM D-6350) and by atomic absorption spectroscopy (ASTM D-5954).

3.3.3. Density

The density of light hydrocarbons can be determined by several methods (ASTM D-1070) including a hydrometer method (ASTM D-1298) and a pressure hydrometer method (ASTM D-1657, IP 235). The specific gravity (relative density) (ASTM D-1070, ASTM D-1657) by itself has little significance compared with its use for higher-molecular-weight liquid petroleum products and can only give an indication of quality characteristics when combined with values for volatility and vapor pressure. It is important for stock quantity calculations and is used in connection with transport and storage.

3.3.4. Sulfur

The manufacturing processes for liquefied petroleum gas are designed so that the majority, if not all, of the sulfur compounds are removed. The total sulfur level is therefore considerably lower than for other petroleum fuels, and a maximum limit for sulfur content helps to define the product more completely. The sulfur compounds that are mainly responsible for corrosion are hydrogen sulfide, carbonyl sulfide, and, sometimes, elemental sulfur. Hydrogen sulfide and mercaptans have distinctive unpleasant odors.

Control of the total sulfur content, hydrogen sulfide, and mercaptans ensures that the product is not corrosive or nauseating. Stipulating a satisfactory copper strip test further ensures control of corrosion.

Total sulfur in gas can be determined by combustion (ASTM D-1072), by the lamp method (ASTM D-1266), or by hydrogenation (ASTM D-3031, ASTM D-4468). Trace total organic and bound nitrogen is determined (ASTM D-4629). The current test method for heavy residues in liquefied petroleum gas (ASTM D-2158) involves evaporation of a liquefied petroleum gas sample, measuring the volume of residue and observing the residue for oil stain on a piece of filter paper.

Corrosive sulfur compounds can be detected by their effect on copper and the form in which the general copper strip corrosion test (ASTM D-l838) for petroleum products is applied to liquefied petroleum gas. Hydrogen sulfide can be detected by its action on moist lead acetate paper, and a procedure is also used as a measure of sulfur compounds. The method follows the principle of the standard Doctor test.

3.3.5. Volatility and Vapor Pressure

The vaporization and combustion characteristics of liquefied petroleum gas are defined for normal applications by volatility, vapor pressure, and, to a lesser extent, specific gravity.

Volatility is expressed in terms of the temperature at which 95% of the sample is evaporated and presents a measure of the least volatile component present (ASTM D-1837). Vapor pressure (IP 410) is, therefore, a measure of the most extreme low-temperature conditions under which initial vaporization can take place. By setting limits on vapor pressure and volatility jointly the specification serves to ensure essentially single-component products for the butane and propane grades (ASTM D-1267, ASTM D-2598, IP 410). By combining vapor pressure/volatility limits with specific gravity for propane-butane mixtures, essentially two-component systems are ensured.

The residue (ASTM D-1025, ASTM D-2158, IP 317), that is, nonvolatile matter, is a measure of the concentration of contaminants boiling above 37.8°C (100°F) that may be present in the gas.

For natural gasoline, the primary criteria are volatility (vapor pressure) and knock performance. Determination of the vapor pressure (ASTM D-323, ASTM D-4953, ASTM D-5190, ASTM D-5191) and distillation profile (ASTM D-216, IP 191) is essential. Knock performance is determined by rating in knock test engines by both the motor method (ASTM D-2700, IP 236) and the research method (ATSM-2699, IP 237). The knock characteristics of liquefied petroleum gases can also be determined (IP 238).

Other considerations for natural gasoline are copper corrosion (ASTM D-130, IP 154, IP 411) and specific gravity (ASTM D-1298, IP 160), the latter determination being necessary for measurement and transportation.

3.3.6. Water

It is a fundamental requirement that liquefied petroleum gas should not contain free water (ASTM D-2713). Dissolved water may give trouble by forming hydrates and giving moisture vapor in the gas phase. Both of these will lead to blockages. Therefore, test methods are available to determine the presence of water using electronic moisture analyzers (ASTM D-5454), dew-point temperature (ASTM D-1142), and length-of-stain detector tubes (ASTM D-4888).

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CHAPTER

4

NAPHTHA

4.1. INTRODUCTION

Naphtha is a liquid petroleum product that boils from about 30°C (86°F) to approximately 200°C (392°F), although there are different grades of naphtha within this extensive boiling range that have different boiling ranges (Guthrie, 1967; Goodfellow, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Speight, 1999; Hori, 2000). The term *petroleum solvent* is often used synonymously with *naphtha*.

On a chemical basis, naphtha is difficult to define precisely because it can contain varying amounts of its constituents (paraffins, naphthenes, aromatics, and olefins) in different proportions, in addition to the potential isomers of the paraffins that exist in the naphtha boiling range (Tables 4.1 and 4.2). Naphtha is also represented as having a boiling range and carbon number similar to those of gasoline (Fig. 4.1), being a precursor to gasoline.

The so-called *petroleum ether* solvents are specific-boiling-range naphtha as is *ligroin*. Thus the term *petroleum solvent* describes special liquid hydrocarbon fractions obtained from naphtha and used in industrial processes and formulations (Weissermel and Arpe, 1978). These fractions are also referred to as *industrial naphtha*. Other solvents include *white spirit*, which is subdivided into *industrial spirit* [distilling between 30°C and 200°C (86°F–392°F)] and *white spirit* [light oil with a distillation range of 135°C–200°C (275°F–392°F)]. The special value of naphtha as a solvent lies in its stability and purity.

In this chapter, references to the various test methods dedicated to the determination of the amounts of carbon, hydrogen, and nitrogen (ASTM D-5291) as well as the determination of oxygen, sulfur, metals, and elements such as chlorine (ASTM D-808) are not included. Such tests might be deemed necessary but, in light of the various tests available for composition, are presumed to be at the discretion of the analyst. References to the various test methods are presented elsewhere (Chapter 2).

Table 4.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

Table 4.2. Increase in the Number of Isomers With Carbon Number

Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

4.2. PRODUCTION AND PROPERTIES

Naphtha is produced by any one of several methods, which include (1) fractionation of straight-run, cracked, and reforming distillates or even fractionation of crude petroleum; (2) solvent extraction; (3) hydrogenation of

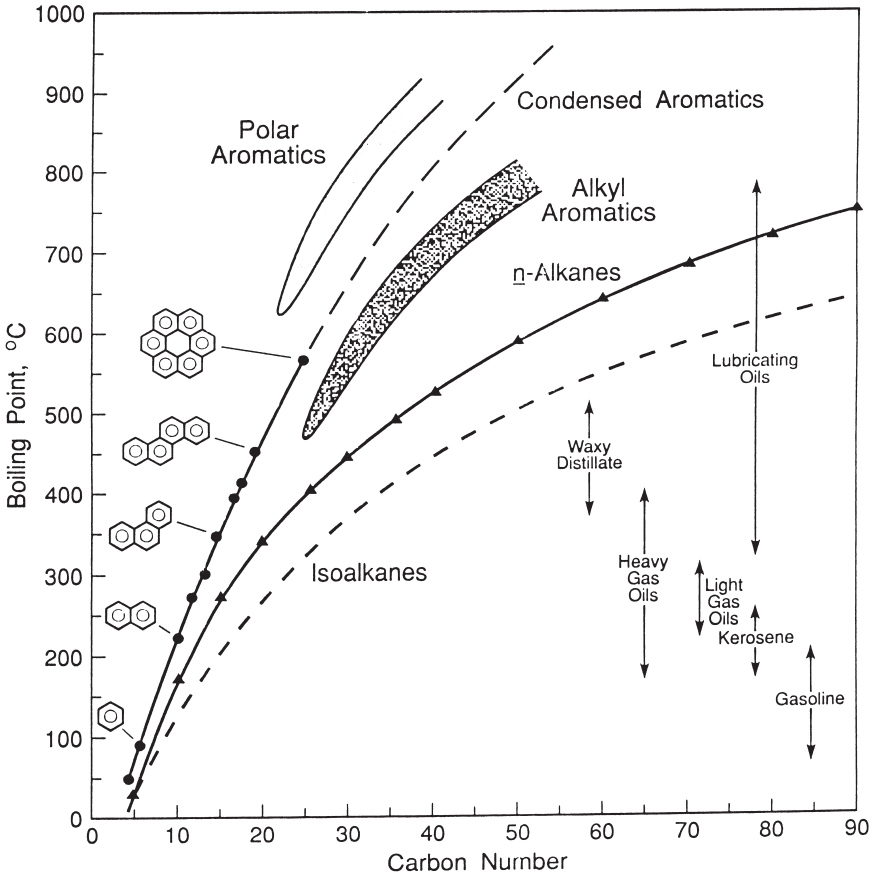

Figure 4.1. Boiling point and carbon number for various hydrocarbons and petroleum products

cracked distillates; (4) polymerization of unsaturated compounds (olefins); and (5) alkylation processes. In fact, naphtha may be a combination of product streams from more than one of these processes.

The more common method of naphtha preparation is distillation. Depending on the design of the distillation unit, either one or two naphtha steams may be produced: (1) a single naphtha with an end point of about 205°C (400°F) and similar to straight-run gasoline or (2) this same fraction divided into a light naphtha and a heavy naphtha. The end point of the light naphtha is varied to suit the subsequent subdivision of the naphtha into narrower boiling fractions and may be of the order of 120°C (250°F).

Sulfur compounds are most commonly removed or converted to a harmless form by chemical treatment with lye, Doctor solution, copper chloride,

or similar treating agents (Speight, 1999). Hydrorefining processes (Speight, 1999) are also often used in place of chemical treatment. When used as a solvent, naphtha is selected for low sulfur content, and the usual treatment processes remove only sulfur compounds. Naphtha with a small aromatic content has a slight odor, but the aromatics increase the solvent power of the naphtha and there is no need to remove aromatics unless odor-free naphtha is specified.

The variety of applications emphasizes the versatility of naphtha. For example, naphtha is used by paint, printing ink and polish manufacturers and in the rubber and adhesive industries as well as in the preparation of edible oils, perfumes, glues, and fats. Further uses are found in the dry-cleaning, leather, and fur industries and also in the pesticide field. The characteristics that determine the suitability of naphtha for a particular use are volatility, solvent properties (dissolving power), purity, and odor (generally, the lack thereof).

To meet the demands of a variety of uses, certain basic naphtha grades are produced that are identified by boiling range. The complete range of naphtha solvents may be divided, for convenience, into four general categories:

1. Special boiling point spirits having overall distillation range within the limits of 30–165°C (86–329°F);
2. Pure aromatic compounds such as benzene, toluene, xylenes, or mixtures (BTX) thereof;
3. White spirit, also known as mineral spirit and naphtha, usually boiling within 150–210°C (302–410°F);
4. High-boiling petroleum fractions boiling within the limits of 160–325°C (320–617°F).

Because the end use dictates the required composition of naphtha, most grades are available in both high- and low-solvency categories and the various text methods can have major significance in some applications and lesser significance in others. Hence the application and significance of tests must be considered in the light of the proposed end use.

Odor is particularly important because, unlike most other petroleum liquids, many of the manufactured products containing naphtha are used in confined spaces, in factory workshops, and in the home.

4.3. TEST METHODS

Because of the high standards set for naphtha (McCann, 1998) it is essential to employ the correct techniques when taking samples for testing

(ASTM D-270, ASTM D-4057, IP 51). Mishandling, or the slightest trace of contaminant, can give rise to misleading results. Special care is necessary to ensure that containers are scrupulously clean and free from odor. Samples should be taken with the minimum of disturbance so as to avoid loss of volatile components; in the case of low-boiling naphtha it may be necessary to chill the sample. And, while awaiting examination samples should be kept in a cool dark place so as to ensure that they do not lose volatile constituents or discolor and develop odors because of oxidation.

The physical properties of naphtha depend on the hydrocarbon types present, in general the aromatic hydrocarbons having the highest solvent power and the straight-chain aliphatic compounds the lowest. The solvent properties can be assessed by estimating the amount of the various hydrocarbon types present. This method provides an indication of the solvent power of the naphtha on the basis that aromatic constituents and naphthenic constituents provide dissolving ability that paraffinic constituents do not. Another method for assessing the solvent properties of naphtha measures the performance of the fraction when used as a solvent under specified conditions such as, for example, by the kauri-butanol test method (ASTM D-l133). Another method involves measurement of the surface tension from which the solubility parameter is calculated and then provides an indication of dissolving power and compatibility. Such calculations have been used to determine the yield of asphaltenes from petroleum by use of various solvents (Mitchell and Speight, 1973; Speight, 1999; Speight, 2001). A similar principle is applied to determine the amount of insoluble material in lubricating oil using *n*-pentane (ASTM D-893, ASTM D-4055).

Insoluble constituents in lubricating oil can cause wear that can lead to equipment failure. Pentane-insoluble materials can include oil-insoluble materials and some oil-insoluble resinous matter originating from oil or additive degradation or both. Toluene-insoluble constituents arise from external contamination, fuel carbon, and highly carbonized materials from degradation of fuel, oil, and additives or engine wear and corrosion materials. A significant change in pentane- or toluene-insoluble constituents indicates a change in oil properties that could lead to machinery failure. The insoluble constituents measured can also assist in evaluating the performance characteristics of a used oil or in determining the cause of equipment failure.

Thus one test (ASTM D-893) covers the determination of pentane- and toluene-insoluble constituents in used lubricating oils with pentane dilution and centrifugation as the method of separation. The other test (ASTM D-4055) uses pentane dilution followed by membrane filtration to remove insoluble constituents that have a size greater than 0.8 μm.

4.3.1. Aniline Point and Mixed Aniline Point

The test method for the determination of aniline point and mixed aniline point of hydrocarbon solvents (ASTM D-611, IP 2) is a means for determining the solvent power of naphtha by estimating of the relative amounts of the various hydrocarbon constituents. It is a more precise technique than the method for kauri-butanol number (ASTM D-1133).

The aniline (or mixed aniline) (ASTM D-611, IP 2) point helps in characterization of pure hydrocarbons and in their mixtures and is most often used to estimate the aromatic content of naphtha. Aromatic compounds exhibit the lowest aniline points and paraffin compounds have the highest aniline points, with cycloparaffins (naphthenes) and olefins having aniline points between the two extremes. In any homologous series the aniline point increases with increasing molecular weight.

There are five submethods in the test (ASTM D-611, IP 2) for the determination of the aniline point: (1) Method A is used for transparent samples with an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture; (2) method B, a thin-film method, is suitable for samples too dark for testing by method A; (3) methods C and D are used when there is the potential for sample vaporization at the aniline point; (4) method D is particularly suitable where only small quantities of sample are available; and (5) method E uses an automatic apparatus suitable for the range covered by methods A and B.

The results obtained by the kauri-butanol test (ASTM D-1133) depend on factors other than solvent power and are specific to the solute employed. For this reason, the aniline point is often preferred to the kauri-butanol number.

4.3.2. Composition

The number of potential hydrocarbon isomers in the naphtha boiling range (Tables 4.1 and 4.2) renders complete speciation of individual hydrocarbons impossible for the naphtha distillation range, and methods are used that identify the hydrocarbon types as chemical groups rather than as individual constituents.

The data from the density (specific gravity) test method (ASTM D-1298, IP 160) provides a means of identification of a grade of naphtha but is not a guarantee of composition and can only be used to indicate evaluate product composition or quality when used in conjunction with the data from other test methods. Density data are used primarily to convert naphtha volume to a weight basis, a requirement in many of the industries concerned. For the necessary temperature corrections and also for volume

corrections the appropriate sections of the petroleum measurement tables (ASTM D-l250, IP 200) are used.

The first level of compositional information is group-type totals as deduced by adsorption chromatography (ASTM D-1319, IP 156) to give volume percentage of saturates, olefins, and aromatics in materials that boil below 315°C (600°F).

In this test method, a small amount of sample is introduced into a glass adsorption column packed with activated silica gel, of which a small layer contains a mixture of fluorescent dyes. When the sample has been adsorbed on the gel, alcohol is added to desorb the sample down the column and the hydrocarbon constituents are separated according to their affinities into three types (aromatics, olefins, and saturates). The fluorescent dyes also react selectively with the hydrocarbon types and make the boundary zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

Other test methods are available. Content of benzene and other aromatics may be estimated by spectrophotometric analysis (ASTM D-1017) and also by gas-liquid chromatography (ASTM D-2267, ASTM D-2600, IP 262). However, two test methods based on the adsorption concept (ASTM D-2007, ASTM D-2549) are used for classifying oil samples of initial boiling point of at least 200°C (392°F) into the hydrocarbon types of polar compounds, aromatics, and saturates and recovery of representative fractions of these types. Such methods are unsuitable for the majority of naphtha samples because of volatility constraints.

An indication of naphtha composition may also be obtained from the determination of aniline point (ASTM D-1012, IP 2), freezing point (ASTM D-852, ASTM D-1015, ASTM D-1493) (Fig. 4.2), cloud point (ASTM D-2500) (Fig. 4.3), and solidification point (ASTM D-1493). And, although refinery treatment should ensure no alkalinity and acidity (ASTM D-847, ASTM D-1093, ASTM D-1613, ASTM D-2896, IP 1) and no olefins present, the relevant tests using bromine number (ASTM D-875, ASTM D-1159, IP 130), bromine index (ASTM D-2710), and flame ionization absorption (ASTM D-1319, IP 156) are necessary to ensure low levels (at the maximum) of hydrogen sulfide (ASTM D-853) as well as the sulfur compounds in general (ASTM D-l30, ASTM D-849, ASTM D-1266, ASTM D-2324, ASTM D-3120, ASTM D-4045, ASTM D-6212, IP 107, IP 154) and especially corrosive sulfur compounds such as are determined by the Doctor test method (ASTM D-4952, IP 30).

Aromatic content is a key property of low-boiling distillates such as naphtha and gasoline because the aromatic constituents influence a variety of properties including boiling range (ASTM D-86, IP 123), viscosity (ASTM D-88, ASTM D-445, ASTM D-2161, IP 71), stability (ASTM D-525, IP 40), and compatibility (ASTM D-1133) with a variety of solutes.

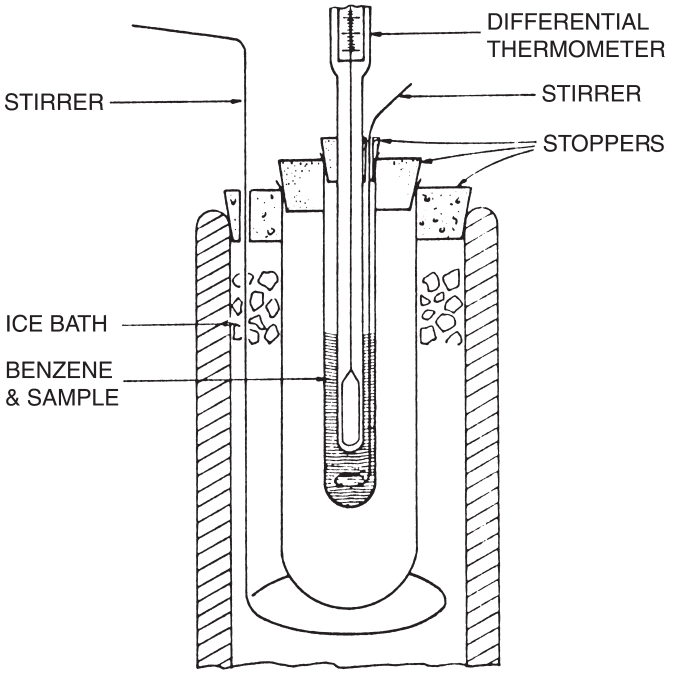

Figure 4.2. Freezing point apparatus for use in the depression of the freezing point of benzene test

Existing methods use physical measurements and require suitable standards. Tests such as aniline point (ASTM D-611) and kauri-butanol number (ASTM D-1133) are of a somewhat empirical nature and can serve a useful function as control tests. Naphtha composition, however, is monitored mainly by gas chromatography, and although most of the methods may have been developed for gasoline (ASTM D-2427, ASTM D-6296), the applicability of the methods to naphtha is sound.

A multidimensional gas chromatographic method (ASTM D-5443) provides for the determination of paraffins, naphthenes, and aromatics by carbon number in low olefinic hydrocarbon streams having final boiling points lower than 200°C (392°F). In this method, the sample is injected into a gas chromatographic system that contains a series of columns and switching values. First a polar column retains polar aromatic compounds, binaphthenes, and high-boiling paraffins and naphthenes. The eluant from this column goes through a platinum column that hydrogenates olefins and then to a molecular sieve column that performs a carbon number separation based on the molecular structure, that is, naphthenes and paraffins. The fraction remaining on the polar column is further divided into three separate

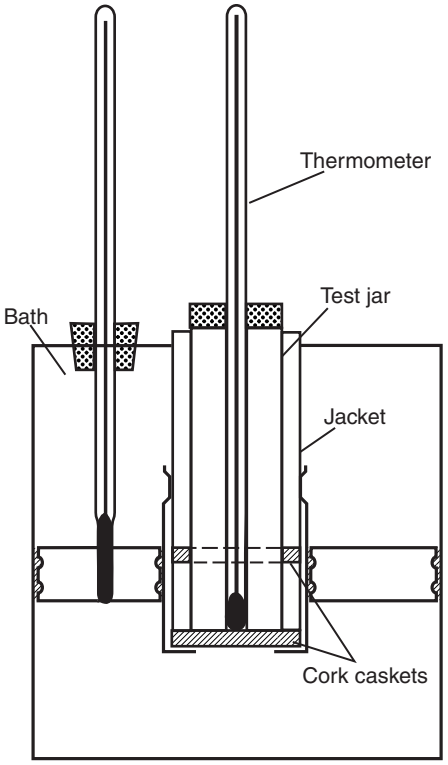

Figure 4.3. Apparatus for the determination of cloud point and pour point

fractions that are then separated on a nonpolar column by boiling point. A flame ionization detector detects eluting compounds.

In another method (ASTM D-4420) for the determination of the amount of aromatic constituents, a two-column chromatographic system connected to a dual-filament thermal conductivity detector (or two single-filament detectors) is used. The sample is injected into the column containing a polar liquid phase. The nonaromatics are directed to the reference side of the detector and vented to the atmosphere as they elute. The column is back-flushed immediately before the elution of benzene, and the aromatic portion is directed into the second column containing a nonpolar liquid phase. The aromatic components elute in the order of their boiling points and are detected on the analytical side of the detector. Quantitation is achieved by utilizing peak factors obtained from the analysis of a sample having a known aromatic content.

Other methods for the determination of aromatics in naphtha include a method (ASTM D-5580) using a flame ionization detector and methods in

which a combination of gas chromatography and Fourier transform infrared spectroscopy (GC-FTIR) (ASTM D-5986) and gas chromatography and mass spectrometry (GC-MS) (ASTM D-5769) is used.

Hydrocarbon composition is also determined by mass spectrometry—a technique that has seen wide use for hydrocarbon-type analysis of naphtha and gasoline (ASTM D-2789) as well as identification of hydrocarbon constituents in higher-boiling naphtha fractions (ASTM D-2425).

One method (ASTM D-6379, IP 436) is used to determine the monoaromatic and diaromatic hydrocarbon contents in distillates boiling in the range from 50 to 300°C (122–572°F). In this method the sample is diluted with an equal volume of hydrocarbon, such as heptane, and a fixed volume of this solution is injected into a high-performance liquid chromatograph fitted with a polar column where separation of the aromatic hydrocarbons from the nonaromatic hydrocarbons occurs. The separation of the aromatic constituents appears as distinct bands according to ring structure, and a refractive index detector is used to identify the components as they elute from the column. The peak areas of the aromatic constituents are compared with those obtained from previously run calibration standards to calculate the % w/w monoaromatic hydrocarbon constituents and diaromatic hydrocarbon constituents in the sample.

Compounds containing sulfur, nitrogen, and oxygen could possibly interfere with the performance of the test. Monoalkenes do not interfere, but conjugated di- and polyalkenes, if present, may interfere with the test performance.

Another method (ASTM D-2425) provides more compositional detail (in terms of molecular species) than chromatographic analysis, and the hydrocarbon types are classified in terms of a Z-series in which Z (in the empirical formula C_nH_{2n+Z}) is a measure of the hydrogen deficiency of the compound. This method requires that the sample be separated into saturate and aromatic fractions before mass spectrometric analysis (ASTM D-2549), and the separation is applicable to some fractions but not others. For example, the method is applicable to high-boiling naphtha but not to low-boiling naphtha because it is impossible to evaporate the solvent used in the separation without also losing the lower-boiling constituents of the naphtha under investigation.

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined by high-resolution nuclear magnetic resonance spectroscopy (ASTM D-5292) that gives the mole percent of aromatic hydrogen or carbon atoms. Proton (hydrogen) magnetic resonance spectra are obtained on sample solutions in either chloroform or carbon tetrachloride with a continuous wave or pulse Fourier transform high-resolution magnetic resonance spectrometer. Carbon magnetic resonance spectra are

obtained on the sample solution in chloroform-*d* with a pulse Fourier transform high-resolution magnetic resonance.

The data obtained by this method (ASTM D-5292) can be used to evaluate changes in aromatic contents in naphtha as well as kerosene, gas oil, mineral oil, and lubricating oil. However, results from this test are not equivalent to mass- or volume-percent aromatics determined by the chromatographic methods because the chromatographic methods determine the percent by weight or percent by volume of molecules that have one or more aromatic rings and alkyl substituents on the rings will contribute to the percentage of aromatics determined by chromatographic techniques.

Low-resolution nuclear magnetic resonance spectroscopy can also be used to determine percent by weight hydrogen in jet fuel (ASTM D-3701) and in light distillate, middle distillate, and gas oil (ASTM D-4808). As noted above, chromatographic methods are not applicable to naphtha where losses can occur by evaporation.

The nature of the uses found for naphtha demands compatibility with the many other materials employed in formulation, waxes, pigments, resins, etc.; thus the solvent properties of a given fraction must be carefully measured and controlled. For most purposes volatility is important, and, because of the wide use of naphtha in industrial and recovery plants, information on some other fundamental characteristics is required for plant design.

Although the focus of many tests is analysis of the hydrocarbon constituents of naphtha and other petroleum fractions, heteroatoms compounds that contain sulfur and nitrogen atoms cannot be ignored and methods for their determination are available. The combination of gas chromatography with element-selective detection gives information about the distribution of the element. In addition, many individual heteroatomic compounds can be determined.

Nitrogen compounds in middle distillates can be selectively detected by chemiluminescence. Individual nitrogen compounds can be detected down to 100 ppb nitrogen. Gas chromatography with either sulfur chemiluminescence detection or atomic emission detection has been used for sulfur selective detection.

Estimates of the purity of these products are determined in laboratories with a variety of procedures such as freezing point, flame ionization absorbance, ultraviolet absorbance, gas chromatography, and capillary gas chromatography (ASTM D-850, ASTM D-852, ASTM D-853, ASTM D-848, ASTM D-849, ASTM D-1015, ASTM D-1016, ASTM D-1078, ASTM D-1319, ASTM D-2008, ASTM D-22368, ASTM D-2306, ASTM D-2360, ASTM D-5917, IP 156).

Gas chromatography (GC) has become a primary technique for determining hydrocarbon impurities in individual aromatic hydrocarbons and

the composition of mixed aromatic hydrocarbons. Although a measure of purity by gas chromatography is often sufficient, gas chromatography is not capable of measuring absolute purity; not all possible impurities will pass through the gas chromatography column, and not all those that do will be measured by the detector. Despite some shortcomings, gas chromatography is a standard, widely used technique and is the basis of many current test methods for aromatic hydrocarbons (ASTM D-2306 ASTM D-2360, ASTM D-3054, ASTM D-3750, ASTM D-3797, ASTM D-3798, ASTM D-4492, ASTM D-4534, ASTM D-4735, ASTM D-5060, ASTM D-5135, ASTM D-5713, ASTM D-5917, ASTM D-6144).

When classes of hydrocarbons, such as olefins, need to be measured, techniques such as bromine index are used (ASTM D-1492, ASTM D-5776).

Impurities other than hydrocarbons are of concern in the petroleum industry. For example, many catalytic processes are sensitive to sulfur contaminants. Consequently, there is also a series of methods to determine trace concentrations of sulfur-containing compounds (ASTM D-1685, ASTM D-3961, ASTM D-4045, ASTM D-4735).

Chloride-containing impurities are determined by various test methods (ASTM D-5194, ASTM D-5808, ASTM D-6069) that have sensitivity to 1 mg/kg, reflecting the needs of industry to determine very low levels of these contaminants.

Water is a contaminant in naphtha and should be measured using the Karl Fischer method (ASTM E-203, ASTM D-1364, ASTM D-1744, ASTM D-4377, ASTM D-4928, ASTM D-6304), by distillation (ASTM D-4006), or by centrifugation (ASTM D-96) and excluded by relevant drying methods.

Tests should also be carried out for sediment if the naphtha has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the naphtha and the resulting products. Test methods are available for the determination of sediment by extraction (ASTM D-473, IP 285) or by membrane filtration (ASTM D-4807, IP 286) and the determination of sediment simultaneously with water by centrifugation (ASTM D-96, ASTM D-1796, ASTM D-2709, ASTM D-4007, IP 373, IP 374).

4.3.3. Correlative Methods

Correlative methods have long been used as a way of dealing with the complexity of various petroleum fractions, including naphtha. Relatively easy to measure physical properties such as density (or specific gravity) (ASTM D-2935 ASTM D-3505, ASTM D-4052) are also required. Viscosity (ASTM D-88, ASTM D-445, ASTM D-2161, IP 71), density (ASTM D-287, ASTM D-891, ASTM D-941, ASTM D-1217, ASTM D-1298, ASTM D-1555, ASTM D-1657, ASTM D-2935, ASTM D-4052, ASTM D-5002, IP 160,

Table 4.3. Refractive Index of Selected Hydrocarbons

Compound	Refractive Index n_D^{20}
n-Pentane	1.3578
n-Hexane	1.3750
n-Hexadecane	1.4340
Cyclopentane	1.4065
Cyclopentene	1.4224
Pentene-1	1.3714
1,3-Pentadiene	1.4309
Benzene	1.5011
cis-Decahydronaphthalene	1.4814
Methylnaphthalenes	1.6150

Table 4.4. Physical Properties of Selected Petroleum Products

Refractive Index n_D^{20}	Specific Gravity 60°/60°F	Viscosity, cSt		Molecular Weight
		100°F	210°F	
1.5185	0.9250	26.35	3.87	300
1.4637	0.8406	14.55	3.28	353
1.5276	0.9367	1955.00	49.50	646
1.4799	0.8724	3597.00	27.35	822

IP 235, IP 365), and refractive index (ASTM D-1218) have been correlated to hydrocarbon composition (Tables 4.3 and 4.4).

4.3.4. Density (Specific Gravity)

Density (the mass of liquid per unit volume at 15°C) and the related terms *specific gravity* (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) and *relative density* (same as *specific gravity*) are important properties of petroleum products as they are a part of product sales specifications, although they only play a minor role in studies of product composition. Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.

The determination of density (specific gravity) (ASTM D-287, ASTM D-891, ASTM D-941, ASTM D-1217, ASTM D-1298, ASTM D-1555, ASTM D-1657, ASTM D-2935, ASTM D-4052, ASTM D-5002, IP 160, IP 235, IP 365) (Fig. 4.4) provides a check on the uniformity of the naphtha and permits calculation of the weight per gallon. The temperature at which the

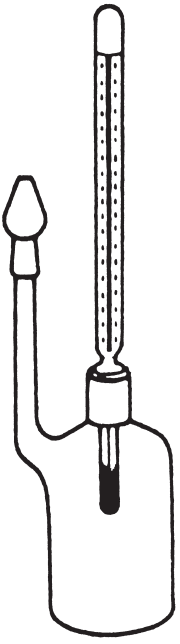

Figure 4.4. Density weighing bottle

determination is carried out and for which the calculations are to be made should also be known (ASTM D-1086). However, the methods are subject to vapor pressure constraints and are used with appropriate precautions to prevent vapor loss during sample handling and density measurement. In addition, some test methods should not be applied if the samples are so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty. The presence of such bubbles can have serious consequences for the reliability of the test data.

4.3.5. Evaporation Rate

The evaporation rate is an important property of naphtha, and although there is a significant relation between distillation range and evaporation rate, the relationship is not straightforward.

A simple procedure for determining the evaporation rate involves use of at least a pair of tared shallow containers, each containing a weighed amount of naphtha. The cover-free containers are placed in a temperature- and humidity-controlled draft-free area. The containers are reweighed at intervals until the samples have completely evaporated or have left a

residue that does not evaporate further (ASTM D-381, ASTM D-1353, IP 131).

The evaporation rate can be derived either (1) by a plot of time versus weight using a solvent having a known evaporation rate for comparison or (2) from the distillation profile (ASTM D-86, IP 123).

4.3.6. Flash Point

The flash point is the lowest temperature at atmospheric pressure (760 mmHg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. Flash point data are used in shipping and safety regulations to define *flammable* and *combustible* materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively nonvolatile or nonflammable material.

Of the available test methods, the most common method of determining the flash point confines the vapor (closed cup method) until the instant the flame is applied (ASTM D-56, ASTM D-93, ASTM D-3828, 6450, IP 34, IP 94, IP 303) (Fig. 4.5). An alternate method that does not confine the vapor

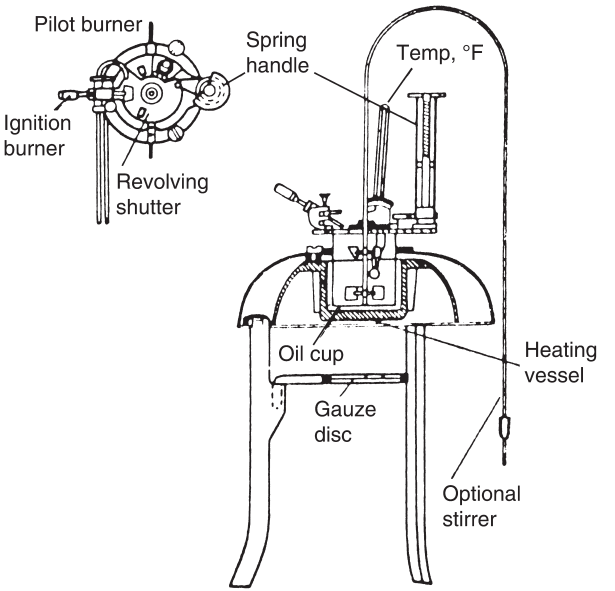

Figure 4.5. Pensky-Marten's flash point apparatus (ASTM D-56)

(open cup method) (ASTM D-92, ASTM D-1310, IP 36) gives slightly higher values of the flash point.

Erroneously high flash points can be obtained when precautions are not taken to avoid the loss of volatile material. Samples should not be stored in plastic bottles, because the volatile material may diffuse through the walls of the container. The containers should not be opened unnecessarily. The samples should not be transferred between containers unless the sample temperature is at least 20°F (11°C) below the expected flash point.

Another test (ASTM E-659) that can be used as a complement to the flash point test involves determination of the auto-ignition temperature. However, the flash point should not be confused with auto-ignition temperature, which measures spontaneous combustion with no external source of ignition.

4.3.7. Kauri-Butanol Value

The kauri-butanol value (ASTM D-1133) is the number of milliliters of the solvent, at 15°C (77°F), required to produce a defined degree of turbidity when added to 20 g of a standard solution of gum kauri resin in *n*-butyl alcohol. The kauri-butanol value of naphtha is used to determine relative solvent power.

For kauri-butanol values of 60 and higher, the standard is toluene, which has an assigned value of 105, whereas for kauri-butanol values less than 60, the standard is a blend of 75% *n*-heptane and 25% toluene, which has an assigned value of 40. The kauri-butanol value of products that are classified as regular mineral spirits normally varies between 34 and 44; xylene is 93, and aromatic naphtha falls in the range 55–108.

However, the data obtained by the kauri-butanol test depend on factors other than solvent power and are specific to the solute used. For this reason, the aniline point is often preferred to the kauri-butanol number.

4.3.8. Odor and Color

The degree of purity of naphtha is an important aspect of naphtha properties, and strict segregation of all distribution equipment is maintained to ensure strict and uniform specification for the product handled. Naphtha is refined to a low level of odor to meet the specifications for use.

In general the paraffinic hydrocarbons possess the mildest odor and the aromatics the strongest, the odor level (ASTM D-268, ASTM D-1296, IP 89) being related to the chemical character and volatility of the constituents. Odors caused by the presence of sulfur compounds or unsaturated constituents are excluded by specification. And apart from certain high-boiling aromatic fractions, which are usually excluded by volatility from the major-

ity of the naphtha fractions, which may be pale yellow in color, naphtha is usually colorless (water white).

Measurement of color (ASTM D-l56, ASTM D-848, ASTM D-1209, ASTM D-1555, ASTM D-5386, IP 17) provides a rapid method of checking the degree of freedom from contamination. Observation of the test for residue on evaporation (ASTM D-381, ASTM D-1353, IP 131) provides a further guard against adventitious contamination.

4.3.9. Volatility

Distillation, as a means of determining the boiling range (hence the *volatility*) of petroleum and petroleum products, has been in use since the beginning of the petroleum industry and is an important aspect of product specifications.

Thus one of the most important physical parameters is the boiling range distribution (ASTM D-86, ASTM D-1078, ASTM D-2887, ASTM D-2892, IP 123). The significance of the distillation test is the indication of volatility, which dictates the evaporation rate, an important property for naphtha used in coatings and similar applications where the premise is that the naphtha evaporates over time, leaving the coating applied to the surface.

In the basic test method (ASTM D-86, IP 123) a 100-ml sample is distilled (manually or automatically) under prescribed conditions. Temperatures and volumes of condensate are recorded at regular intervals, from which the boiling profile is derived.

The determination of the boiling range distribution of distillates such as naphtha and gasoline by gas chromatography (ASTM D-3710) not only helps identify the constituents but also facilitates on-line controls at the refinery. This test method is designed to measure the entire boiling range of naphtha with either high or low Reid vapor pressure (ASTM D-323, IP 69). In this method, the sample is injected into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Calibration is performed with a known mixture of hydrocarbons covering the expected boiling range of the sample.

Another method is described as a method for determining the carbon number distribution (ASTM D-2887, IP 321), and the data derived by this test method are essentially equivalent to those obtained by true boiling point (TBP) distillation (ASTM D-2892). The sample is introduced into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve obtained under

the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution may be obtained. However, this test method is limited to samples with a boiling range greater than 55°C (100°F) and having a vapor pressure (ASTM D-323, ASTM D-4953, ASTM D-5190, ASTM D-5191, ASTM D-5482, ASTM D-6377, ASTM D-6378, IP 69, IP 394) sufficiently low to permit sampling at ambient temperature.

Naphtha grades are often referred to by boiling points, that is, the defined temperature range in which the fraction distills. The ranges are determined by standard methods (ASTM D-8, ASTM D-107, IP 123, IP 195), it being especially necessary to use a recognized method because the initial and final boiling points, which ensure conformity with volatility requirements and absence of *heavy ends*, are themselves affected by the testing procedure.

A simple test for the evaporation properties of naphtha is available (ASTM D-381, IP 131), but the volatility of naphtha is generally considered a measure of its drying time in use. And the temperature of use obviously governs the choice of naphtha. A high- boiling narrow distillation fraction of gas oil may be required for a heat-set ink, where the operating temperature may be as high as 316°C (600°F). However, the need for vacuum distillation (ASTM D-1160) as a product specification in the boiling range of naphtha is not necessary. By definition, naphtha very rarely has such a high boiling point.

Although pure hydrocarbons such as pentane, hexane, heptane, benzene, toluene, and xylene, which are now largely of petroleum origin, may be characterized by a fixed boiling point, naphtha is a mixture of many hydrocarbons and cannot be so identified. The distillation test does, however, give a useful indication of their volatility. The data obtained should include the initial and final temperatures of distillation together with sufficient temperature and volume observations to permit a characteristic distillation curve to be drawn.

This information is especially important when a formulation includes other volatile liquids because the performance of the product will be affected by the relative volatility of the constituents. An illustration of the importance of this aspect is found in the use of specifically defined boiling point naphtha in cellulose lacquers, where a mixture with ester, alcohols, and other solvents may be employed. The naphtha does not act as a solvent for the cellulose ester but is incorporated as a diluent to control the viscosity and flow properties of the mixture. If the solvent evaporates too rapidly blistering and pimpling of the surface coating may result, whereas if the solvent evaporates unevenly, leaving behind a higher proportion of the naphtha, precipitation of the cellulose may occur, leading to a milky opaqueness known as blushing.

Although much dependence is placed on the assessment of volatility by distillation methods, some specifications include measurement of drying time by evaporation from a filter paper or dish. Laboratory measurements are expressed as *evaporation rate* either by reference to a pure compound evaporated under conditions similar to those for the sample under test or by constructing a time-weight loss curve under standard conditions. Although the results obtained on the naphtha provide a useful guide, it is better, wherever possible, to carry out a performance test on the final product when assessing formulations.

In choosing naphtha for a particular purpose it is necessary to relate volatility to the fire hazard associated with its use, storage, and transport and also with the handling of the products arising from the process. This is normally based on the characterization of the solvent by flash point limits (ASTM D-56, ASTM D-93, IP 34, IP 170).

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CHAPTER

5

GASOLINE

5.1. INTRODUCTION

Gasoline (also referred to as *motor gasoline, petrol* in Britain, *benzine* in Europe) is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum that is used as fuel for internal combustion engines such as occur in motor vehicles, excluding aircraft (Guthrie, 1967; Boldt and Griffiths, 1973; Weissermel and Arpe, 1978; Francis, and Peters, 1980; Hoffman, 1983; Austin, 1984; Hoffman and McKetta, 1993; McCann, 1998; Speight, 1999).

The boiling range of motor gasoline falls between –1°C (30°F) and 216°C (421°F) and has the potential to contain several hundred isomers of the various hydrocarbons (Tables 5.1 and 5.2)—a potential that may be theoretical and never realized in practice (Gruse and Stevens, 1960). The hydrocarbon constituents in this boiling range are those that have 4–12 carbon atoms in their molecular structure and fall into three general types: (1) paraffins (including the cycloparaffins and branched materials), (2) olefins, and (3) aromatics. Gasoline boils at about the same range as naphtha (a precursor to gasoline) but below kerosene (Fig. 5.1).

The various test methods dedicated to the determination of the amounts of carbon, hydrogen, and nitrogen (ASTM D-5291) as well as the determination of oxygen, sulfur, metals, and chlorine (ASTM D-808) are not included in this discussion. Although necessary, the various tests available for composition (Chapter 2) are left to the discretion of the analyst. In addition, test methods recommended for naphtha (Chapter 4) may also be applied, in many circumstances, to gasoline.

5.2. PRODUCTION AND PROPERTIES

Gasoline was at first produced by distillation, simply separating the volatile, more valuable fractions of crude petroleum, and was composed of the naturally occurring constituents of petroleum. Later processes, designed to raise the yield of gasoline from crude oil, split higher-molecular-weight constituents into lower-molecular-weight products by processes known as

Table 5.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

Table 5.2. Increase in the number of Isomers with Carbon Number

Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

cracking. And, like typical gasoline, several processes (Table 5.3) produce the blending stocks for gasoline.

By way of definition of some of these processes, *polymerization* is the conversion of gaseous olefins such as propylene and butylene into larger molecules in the gasoline range.

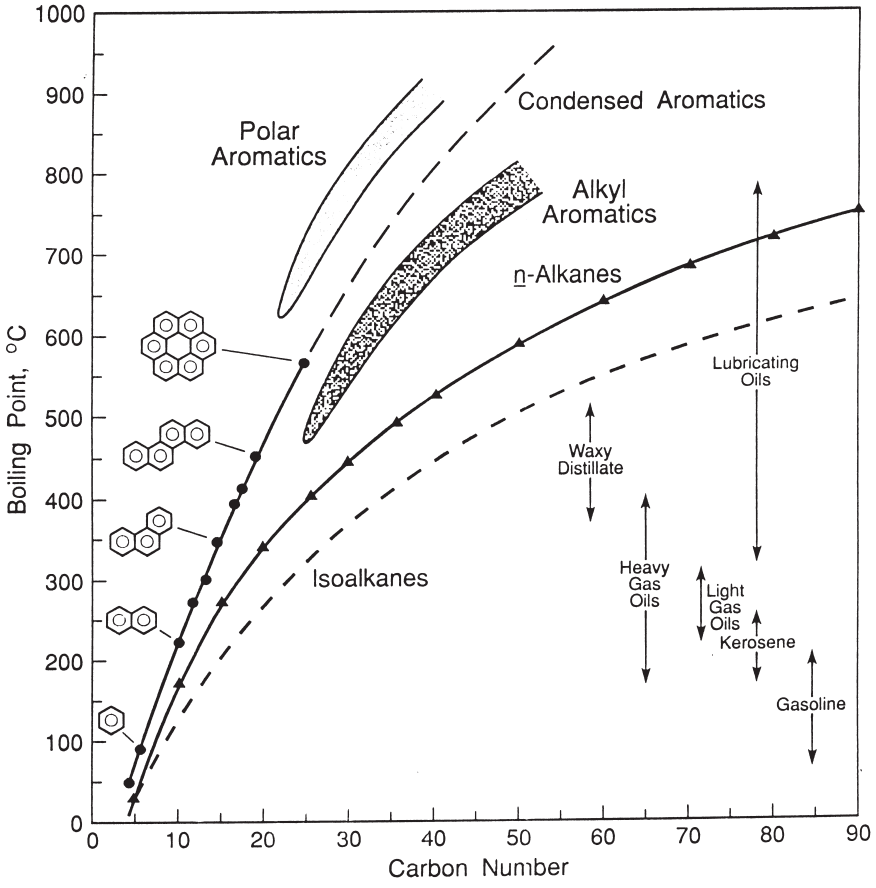

Figure 5.1. Boiling point and carbon number for various hydrocarbons and petroleum products

$$CH_3CH{=}CH_2 + CH_3CH_2CH{=}CH_2\ (+\ H_2) \rightarrow CH_3CH_2CH_2CH_2CH(CH_3)CH_3$$

A*lkylation* is a process combining an olefin and a paraffin (such as *iso*-butane).

$$CH_3CH{=}CH_2 + (CH_3)_3CH \rightarrow CH_3CHCH_2CH(CH_3)_2CH_3$$

Isomerization is the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons).

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$$

Table 5.3. Component Streams and Processes for Gasoline Production

Stream	Producing Process	Boiling Range	
		°C	°F
Paraffinic			
Butane	Distillation Conversion	0	32
Isopentane	Distillation Conversion Isomerization	27	81
Alkylate	Alkylation	40–150	105–300
Isomerate	Isomerization	40–70	105–160
Straight-run naphtha	Distillation	30–100	85–212
Hydrocrackate	Hydrocracking	40–200	105–390
Olefinic			
Catalytic naphtha	Catalytic cracking	40–200	105–390
Steam-cracked naphtha	Steam cracking	40–200	105–390
Polymer	Polymerization	60–200	140–390
Aromatic			
Catalytic reformate	Catalytic reforming	40–200	105–390

Reforming is the use of either heat or a catalyst to rearrange the molecular structure. Selection of the components and their proportions in a blend is the most complex problem in a refinery.

$$\underset{\text{cydohexane}}{C_6H_{12}} \rightarrow \underset{\text{benzene}}{C_6H_6}$$

Thus gasoline is a mixture of hydrocarbons that boils below 180°C (355°F) or, at most, below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have 4–12 carbon atoms in their molecular structure. The hydrocarbons of which gasoline is composed fall into three general types: paraffins (including the cycloparaffins and branched materials), olefins, and aromatics.

The hydrocarbons produced by modern refining techniques (distillation, cracking, reforming, alkylation, isomerization, and polymerization) provide blending components for gasoline production (Speight, 1999; Speight and Ozum, 2002).

Gasoline consists of a very large number of different hydrocarbons, and the individual hydrocarbons in gasoline cannot be conveniently used to describe gasoline. The composition of gasoline is best expressed in terms of hydrocarbon types (saturates, olefins, and aromatics) that enable inferences to be made about the behavior in service.

5.3. TEST METHODS

The test protocols used for gasoline are similar to the protocols used for naphtha. The similarity of the two liquids requires the application of similar test methods. However, knocking properties are emphasized for gasoline and there are several other differences that must be recognized. But, all in all, consultation of the test methods used for the analysis of naphtha (Chapter 4) can assist in developing protocols for gasoline.

The properties of gasoline are quite diverse, and the principal properties affecting the performance of gasoline are volatility and combustion characteristics. These properties are adjusted according to the topography and climate of the country in which the gasoline is to be used. For example, mountainous regions will require gasoline with volatility and knock characteristics somewhat different from those that are satisfactory in flat or undulating country only a little above sea level. Similarly, areas that exhibit extremes of climatic temperature, such as the northern provinces of Canada, where temperatures of 30°C (86°F) in the summer are often followed by temperatures as low as –40°C (–40°F) in the winter, necessitate special consideration, particularly with regard to volatility.

Because of the high standards set for gasoline, as with naphtha, it is essential to use the correct techniques when taking samples for testing (ASTM D-270, ASTM D-4057, IP 51). Mishandling, or the slightest trace of contaminant, can give rise to misleading results. Special care is necessary to ensure that containers are scrupulously clean and free from odor. Samples should be taken with the minimum of disturbance so as to avoid loss of volatile components; in the case of the lightest solvents it may be necessary to chill the sample.

While awaiting examination, samples should be kept in a cool dark place so as to ensure that they do not discolor or develop odors.

5.3.1. Additives

Additives are chemical compounds intended to improve some specific properties of gasoline or other petroleum products and can be monofunctional or multifunctional (Table 5.4; ASTM D-2669). Different additives, even when added for identical purposes, may be incompatible with each other and may, for example, react and form new compounds. Consequently, a blend of two or more gasolines, containing different additives, may form a system in which the additives react with each other and so deprive the blend of their beneficial effect.

Thus certain substances added to gasoline, notably the lead alkyls, have a profound effect on antiknock properties and inhibit the precombustion oxidation chain that is known to promote knocking. For a considerable period,

Table 5.4. Additives for Gasoline

Class and Function	Additive Type
Oxidation Inhibitors—minimize oxidation and gum formation	Aromatic amines and hindered phenols
Corrosion Inhibitors—inhibit ferrous corrosion in in pipelines, storage tanks, and vehicle fuel systems	Carboxylic acids and carboxylates
Metal Deactivators—inhibit oxidation and gum formation catalyzed by ions of copper and other metals	Chelating agent
Carburetor/Injector Detergents—prevent and remove deposits in carburetors and port fuel injectors	Amines, amides, and amine carboxylates
Deposit Control Additives—remove and prevent deposits throughout fuel injectors, carburetors, intake ports and valves, and intake manifold	Polybutene amines and polyether amines
Demulsifiers—minimize emulsion formation by improving water separation	Polyglycol derivatives
Anti-Icing Additives—minimize engine stalling and starting problems by preventing ice formation in the carburetor and fuel system	Surfactants, alcohols, and glycols
Antiknock Compounds—improve octane quality of gasoline	Lead alkyls and methylcyclopentadienyl manganese tricarbonyl
Dyes—Identification of gasoline	Oil-soluble solid and liquid dyes

tetraethyl lead (TEL) was the preferred compound, but more recently tetramethyl lead (TML) has been shown to have advantages with certain modern types of gasoline because of its lower boiling point (110°C/230°F as against 200°C/392°F for tetraethyl lead) and therefore its higher vapor pressure, which enables it to be more evenly distributed among the engine cylinders with the more volatile components of the gasoline.

Some gasoline may still contain tetramethyl lead and tetraethyl lead, whereas others contain compounds prepared by a chemical reaction between tetramethyl lead and tetraethyl lead in the presence of a catalyst. These chemically reacted compounds contain various proportions of tetramethyl lead and tetraethyl lead and their intermediates, trimethylethyl lead, dimethyldiethyl lead, and methyltriethyl lead, and thus provide antiknock compounds with a boiling range of 110–200°C (230–392°F). The lead compounds, if used alone, would cause an excessive accumulation of lead compounds in the combustion chambers of the engine and on sparking

plugs and valves. Therefore "scavengers" such as dibromoethane, alone or in admixture with dichloroethane, are added to the lead alkyl and combine with the lead during the combustion process to form volatile compounds that pass harmlessly from the engine.

The amount of lead alkyl compounds used in gasoline is normally expressed in terms of equivalent grams of metallic lead per gallon or per liter. The maximum concentration of lead permitted in gasoline varies from country to country according to governmental legislation or accepted commercial practice, and it is a subject that is currently under discussion in many countries because of the attention being paid to reduction of exhaust emissions from the spark ignition engine.

The total lead in gasoline may be determined gravimetrically (ASTM D-52, IP 96), polarographically (ASTM D-1269), by atomic absorption spectrometry (ASTM D-3237, IP 428), by the iodine chloride method (ASTM D-3341, IP 270), by inductively coupled plasma atomic emission spectrometry (ASTM D-5185), and by X-ray fluorescence (ASTM D-5059). When it is desired to estimate tetraethyl lead a method is available (IP 116), whereas for the separate determination of tetramethyl lead and tetraethyl lead recourse can be made to separate methods (ASTM D-l949, IP 188).

Other additives used in gasoline include antioxidants and metal deactivators for inhibiting gum formation, surface-active agents and freezing point depressants for preventing carburetor icing, deposit modifiers for reducing spark plug fouling and surface ignition, and rust inhibitors (ASTM D-665, IP 135) for preventing the rusting of steel tanks and pipe work by the traces of water carried in gasoline. For their estimation specialized procedures involving chemical tests and physical techniques such as spectroscopy and chromatography have been used successfully.

Test methods have been developed to measure ethers and alcohols in gasoline-range hydrocarbons, because oxygenated components such as *methyl-tert-butylether* and ethanol are common blending components in gasoline (ASTM D-4814, ASTM D-4815, ASTM D-5441, ASTM D-5599, ASTM D-5986 ASTM D-5622, ASTM D-5845, ASTM D-6293).

Another type of gasoline sometimes referred to as *vaporizing oil* or *power kerosene* is primarily intended as a gasoline for agricultural tractors and is, in effect, a low-volatility (higher boiling) gasoline. For reliable operation, such a gasoline must not be prone to deposit formation (sediment or gum) and the residue on evaporation (ASTM D-381, IP 131) must, therefore, be low. The volatility of vaporizing oil is, as for regular gasoline, assessed by the distillation test (ASTM D-86, IP 123), the requirement normally being controlled by the percentages boiling at 160°C and 200°C (320°F and 392°F).

Because of the lower volatility of vaporizing oil compared with that of gasoline, a relatively high proportion of aromatics (ASTM D-4420) may be

necessary to maintain the octane number although unsaturated hydrocarbons may also be used in proportions compatible with stability requirements. However, the presence of unsaturated constituents must be carefully monitored because of the potential for incompatibility through the formation of sediment and gum. Other tests include flash point (closed cup method: ASTM D-56, ASTM D-93, ASTM D-3828, 6450, IP 34, IP 94, IP 303; open cup method: ASTM D-92, ASTM D-1310, IP 36), sulfur content (ASTM D-1266, IP 107), corrosion (ASTM D-l30, ASTM D-849, IP 154), octane number (ASTM D-2699, ASTM D-2700, ASTM D-2885, IP 236, IP 237), and residue on evaporation (ASTM D-381, ASTM D-1353, IP 131).

Although trace elements such as lead (ASTM D-52, ASTM D-1269, ASTM D-3116, ASTM D-3237, ASTM D-3441, ASTM D-5059, ASTM D-5185, IP 96, IP 228, IP 270), manganese (ASTM D-3831), and phosphorus (ASTM D-3231) are not always strictly additives, tests for the presence of these elements must be stringently followed because their presence can have an adverse affect on gasoline performance or on the catalytic converter.

5.3.2. Combustion Characteristics

Combustion in the spark ignition engine depends chiefly on engine design and gasoline quality. Under ideal conditions, the flame initiated at the sparking plug spreads evenly across the combustion space until all the gasoline has been burned. The increase in temperature caused by the spreading of the flame results in an increase in pressure in the end gas zone, which is that part of the gasoline-air mixture that the flame has not yet reached. The increase in temperature and pressure in the end gas zone causes the gasoline to undergo preflame reactions. Among the main preflame products are the highly temperature-sensitive peroxides, and if these exceed a certain critical threshold concentration, the end gas will spontaneously ignite before the arrival of the flame front emanating from the sparking plug; this causes detonation or *knocking*. On the other hand, if the flame front reaches the end gas zone before the buildup of the critical threshold peroxide concentration, the combustion of the gasoline-air mixture will be without *knock*.

The various types of hydrocarbons in gasoline behave differently in their preflame reactions and thus, their tendency to knock. It is difficult to find any precise relationship between chemical structure and antiknock performance in an engine. Members of the same hydrocarbon series may show very different *antiknock* effects. For example, normal heptane and normal pentane, both paraffins, have antiknock ratings (octane numbers) of 0 and 61.9, respectively (Table 5.5). Very generally, aromatic hydrocarbons (e.g., benzene and toluene), highly branched *iso*-paraffins (e.g., *iso*-octane), and

Table 5.5. Octane Numbers of Selected Hydrocarbons

Hydrocarbons	Octane Number	
	Research	Motor
Normal paraffins		
Pentane	61.7	61.9
Hexane	24.8	26.0
Heptane	0.0	0.0
Octane	–19.0	–15.0
Nonane	–17.0	–20.0
Isoparaffins		
2-Methylbutane (isopentane)	92.3	90.3
2-Methylhexane (isoheptane)	42.4	46.4
2-Methylheptane (isooctane)	21.7	23.8
2,4-Dimethylhexene	65.2	69.9
2,2,4-Trimethylpentane (“isooctane”)	100.0	100.0
Olefins		
1-Pentene	90.9	77.1
1-Octene	28.7	34.7
3-Octene	72.5	68.1
4-Methyl-l-pentene	95.7	80.9
Aromatics		
Benzene		114.8
Toluene	120.1	103.5

olefins (e.g., diisobutylene) have high antiknock values. In an intermediate position are *iso*-paraffins with little branching and naphthenic hydrocarbons (e.g., cyclohexane), whereas the normal paraffins (e.g., normal heptane) are of low antiknock value .

The knock rating of a gasoline is expressed as *octane number* and is the percentage by volume of *iso*-octane (octane number 100, by definition) in admixture with normal heptane (octane number 0, by definition) that has the same knock characteristics as the gasoline being assessed.

Gasoline is normally rated by using two sets of conditions of differing severity. One, known as the research method (ASTM D-2699, IP 237), gives a rating applicable to mild operating conditions, that is, low inlet mixture temperature and relatively low engine loading such as would be experienced generally in passenger cars and light-duty commercial vehicles. The other is the motor method (ASTM D-2700, ASTM D-2885, IP 236), which represents more severe operating conditions, that is, relatively high inlet mixture temperature and high engine loading such as would be experienced during full-throttle operation at high speed.

Research octane numbers are generally higher than those obtained by the motor method, and the difference between the two ratings is known as the *sensitivity* of the gasoline. The sensitivity of low-octane-number gasoline is usually small, but with high-octane gasoline it varies greatly according to gasoline composition and for most commercial blends it is between 7 and 12 in the 90–00 research octane number range. The actual performance of a gasoline on the road (the *road octane number*) usually falls between the research and motor values and depends on the engine used and also on the gasoline composition and choice of antiknock compounds.

To avoid the confusion arising from the use of two separate octane number scales, one below and one above 100, an arbitrary extension of the octane number scale was selected so that the value in terms of automotive engine performance of each unit between 100 and 103 was similar to those between 97 and 100. The relationship between the octane number scale above 100 and the performance number scale is:

$$\text{Octane number} = 100 + (\text{performance number} - 100)/3$$

and the relationship between tetraethyl lead concentration in *iso*-octane and octane number is given in various test methods (ASTM D-270, ASTM D-2699, IP 236, IP 237).

The *heat of combustion* (ASTM D-240, ASTM D-2382, IP 12) is a direct measure of gasoline energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of gasoline with oxygen in a standard bomb calorimeter. This gasoline property affects the economics of engine performance, and the specified minimum value is a compromise between the conflicting requirements of maximum gasoline availability and consumption characteristics.

An alternative criterion of energy content is the *aniline gravity product* (AGP), which is fairly accurately related to calorific value but more easily determined. It is the product of the gravity at 60°F (expressed in degrees API) and the aniline point of the gasoline in °F (ASTM D-611, IP 2). The aniline point is the lowest temperature at which the gasoline is miscible with an equal volume of aniline and is inversely proportional to the aromatic content and related to the calorific value (ASTM D-1405, IP 193).

5.3.3. Composition

As with naphtha, the number of potential hydrocarbon isomers in the gasoline boiling range (Table 5.2) renders complete speciation of individual hydrocarbons impossible for the gasoline distillation range, and methods are used that identify the hydrocarbon types as chemical groups rather than as individual constituents.

In terms of hydrocarbon components, several procedures have been devised for the determination of hydrocarbon type, and the method based on fluorescent indicator adsorption (ASTM D-l319, IP 156) is the most widely employed. Furthermore, aromatic content is a key property of low-boiling distillates such as gasoline because the aromatic constituents influence a variety of properties including boiling range (ASTM D-86, IP 123), viscosity (ASTM D-88, ASTM D-445, ASTM D-2161, IP 71), and stability (ASTM D-525, IP 40). Existing methods use physical measurements and need suitable standards. Tests such as aniline point (ASTM D-611) and kauri-butanol number (ASTM D-1133) are of a somewhat empirical nature and can serve a useful function as control tests. However, gasoline composition is monitored mainly by gas chromatography (ASTM D-2427, ASTM D-6296).

A multidimensional gas chromatographic method (ASTM D-5443) provides for the determination of paraffins, naphthenes, and aromatics by carbon number in low olefinic hydrocarbon streams having final boiling points lower than 200°C (392°F). In this method, the sample is injected into a gas chromatographic system that contains a series of columns and switching values. First a polar column retains polar aromatic compounds, binaphthenes, and high-boiling paraffins and naphthenes. The eluant from this column goes through a platinum column that hydrogenates olefins and then to a molecular sieve column that performs a carbon number separation based on the molecular structure, that is, naphthenes and paraffins. The fraction remaining on the polar column is further divided into three separate fractions that are then separated on a nonpolar column by boiling point. A flame ionization detector detects eluting compounds.

In another method (ASTM D-4420) for the determination of the amount of aromatic constituents, a two-column chromatographic system connected to a dual-filament thermal conductivity detector (or two single filament detectors) is used. The sample is injected into the column containing a polar liquid phase. The nonaromatics are directed to the reference side of the detector and vented to the atmosphere as they elute. The column is backflushed immediately before the elution of benzene, and the aromatic portion is directed into the second column containing a nonpolar liquid phase. The aromatic components elute in the order of their boiling points and are detected on the analytical side of the detector. Quantitation is achieved by utilizing peak factors obtained from the analysis of a sample having a known aromatic content. However, the method may be susceptible to errors caused by alkyl-substituted aromatics (Fig. 5.2) where the boiling point increases because of the alkyl side chain and this increase bears little relationship to the aromatic ring.

Other methods for the determination of aromatics in gasoline include a method (ASTM D-5580) using a flame ionization detector and methods in

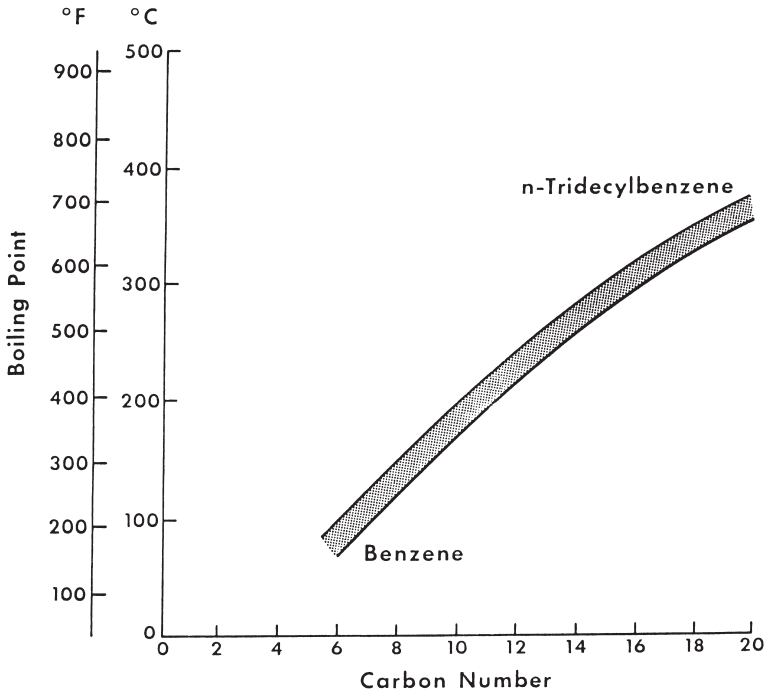

Figure 5.2. Effect of increasing length of the alkyl chain on the boiling point

which a combination of gas chromatography and Fourier transform infrared spectroscopy (GC-FTIR) (ASTM D-5986) and gas chromatography and mass spectrometry (GC-MS) (ASTM D-5769) are used.

The accurate measurements of benzene, and/or toluene, and total aromatics in gasoline are regulated test parameters in gasoline (ASTM D-3606, ASTM D-5580, ASTM D-5769, ASTM D-5986). The precision and accuracy of some of these tests are diminished in gasoline containing ethanol or methanol, because these components often do not completely separate from the benzene peak.

Benzene, toluene, ethylbenzene, the xylene isomers, as well as C_9 aromatics and higher-boiling aromatics are determined by gas chromatography, and the test (ASTM D5580) was developed to include gasoline containing commonly encountered alcohols and ethers. This test is the designated test for determining benzene and total aromatics in gasoline and includes testing gasoline containing oxygenates and uses a flame ionization detector. Another method that employs the flame ionization technique (ASTM D-1319, IP 156) is widely used for measuring total olefins in gasoline fractions as well as aromatics and saturates, although the results

may need correction for the presence of oxygenates. Gas chromatography is also used for the determination of olefins in gasoline (ASTM D-6296).

Benzene in gasoline can also be measured by infrared spectroscopy (ASTM D-4053). But additional benefits are derived from *hyphenated* analytical methods such as gas chromatography-mass spectrometry (ASTM D-5769) and gas chromatography-Fourier transform infrared spectroscopy) ASTM D-5986), which also accurately measure benzene in gasoline. The gas chromatography-mass spectrometry method (ASTM D-5769) is based on the Environmental Protection Agency's gas chromatography/mass spectrometry (EPA GC/MS) procedure for aromatics.

Hydrocarbon composition is also determined by mass spectrometry—a technique that has seen wide use for hydrocarbon-type analysis of gasoline (ASTM D-2789) as well as to the identification of hydrocarbon constituents in higher-boiling gasoline fractions (ASTM D-2425).

One method (ASTM D-6379, IP 436) is used to determine the monoaromatic and diaromatic hydrocarbon contents in distillates boiling in the range from 50 to 300°C (122–572°F). In this method the sample is diluted with an equal volume of hydrocarbon, such as heptane, and a fixed volume of this solution is injected into a high-performance liquid chromatograph fitted with a polar column where separation of the aromatic hydrocarbons from the nonaromatic hydrocarbons occurs. The separation of the aromatic constituents appears as distinct bands according to ring structure, and a refractive index detector is used to identify the components as they elute from the column. The peak areas of the aromatic constituents are compared with those obtained from previously run calibration standards to calculate the % w/w monoaromatic hydrocarbon constituents and diaromatic hydrocarbon constituents in the sample.

Compounds containing sulfur, nitrogen, and oxygen could possibly interfere with the performance of the test. Monoalkenes do not interfere, but conjugated di- and polyalkenes, if present, may interfere with the test performance.

Paraffins, naphthenes, and aromatic hydrocarbons in gasoline and other distillates boiling up to 200°C (392°F) are determined by multidimensional gas chromatography (ASTM D-5443). Olefins that are present are converted to saturates and are included in the paraffin and naphthene distribution. However, the scope of this test does not allow it to be applicable to hydrocarbons containing oxygenates. An extended version of the method can be used to determine the amounts of paraffins, olefins, naphthenes, and aromatics (PONA) in gasoline-range hydrocarbon fractions (ASTM D-6293).

A titration procedure (ASTM D-1159), which determines the bromine number of petroleum distillates and aliphatic olefins by electrometric titration, can be used to provide an approximation of olefin content in a sample. Another related method (ASTM D-2710) is used to determine the bromine

index of petroleum hydrocarbons by electrometric titration and is valuable for determining trace levels of olefins in gasoline. Obviously, these methods use an indirect route to determine the total olefins, and the type of olefinic compound present affects the results because the results depend on the ability of the olefins to react with bromine. Steric factors can prove to have an adverse affect on the experimental data.

The compositional analysis of gasoline, up to and including *n*-nonane, can be achieved using by capillary gas chromatography (ASTM Test Method D5134). Higher-resolution gas chromatography capillary column techniques provide a detailed analysis of most of the individual hydrocarbons in gasoline, including many of the oxygenated blending components. Capillary gas chromatographic techniques can be combined with mass spectrometry to enhance the identification of the individual components and hydrocarbon types.

The presence of pentane and lighter hydrocarbons in gasoline interferes in the determination of hydrocarbon types (ASTM D-1319 and ASTM D-2789). Pentane and lighter hydrocarbons are separated by this test method so that the dependentanized residue can be analyzed, and pentane and lighter hydrocarbons can be analyzed by other methods, if desired. Typically about 2% by volume of pentane and lower-boiling hydrocarbons remain in the bottoms, and hexane and higher-boiling hydrocarbons carry over to the overhead. In this test (ASTM D-2001) a 50-ml sample is distilled into an *overhead* (pentane and lower-boiling hydrocarbons) fraction and a *bottoms* (hexane and higher-boiling hydrocarbons) fraction. The volume of bottoms is measured, and the percent by volume, based on the original gasoline charged to the unit, is calculated.

Sulfur-containing components exist in gasoline-range hydrocarbons and can be identified with a gas chromatographic capillary column coupled with either a sulfur chemiluminescence detector or an atomic emission detector (AED) (ASTM D-5623). The most widely specified method for total sulfur content uses X-ray spectrometry (ASTM D-2622), and other methods that use ultraviolet fluorescence spectroscopy (ASTM D-5453) and/or hydrogenolysis and colorimetry (ASTM D-4045) are also applicable, particularly when the sulfur level is low.

5.3.4. Corrosiveness

Because a gasoline would be unsuitable for use if it corroded the metallic parts of the gasoline system or the engine, it must be substantially free from corrosive compounds both before and after combustion.

Corrosiveness is usually due to the presence of free sulfur and sulfur compounds that burn to form sulfur dioxide (SO_2), which combines with water vapor formed by the combustion of the gasoline to produce sulfurous

acid (H_2SO_3). Sulfurous acid can, in turn, oxidize to sulfuric acid (H_2SO_4), and both acids are corrosive toward iron and steel and would attack the cooler parts of the engine's exhaust system and its cylinders as they cool off after the engine is shut down.

The total sulfur content of gasoline is very low, and knowledge of its magnitude is of chief interest to the refiner who must produce a product that conforms to a stringent specification. Various methods are available for the determination of total sulfur content. The one most frequently quoted in specifications is the *lamp method* (ASTM D-1266, IP 107), in which the gasoline is burned in a small wick-fed lamp in an artificial atmosphere of carbon dioxide and oxygen; the oxides of sulfur are converted to sulfuric acid, which is then determined either volumetrically or gravimetrically.

A more recent development is the Wickbold method (ASTM D-2785, IP 243). This is basically similar to the lamp method except that the sample is burned in an oxy-hydrogen burner to give much more rapid combustion. An alternative technique, which has the advantage of being nondestructive, is X-ray spectrography (ASTM D-2622).

Mercaptan sulfur (R-SH) and hydrogen sulfide (H_2S) (ASTM D-1219, IP 103, IP 104) are undesirable contaminants because, apart from their corrosive nature, they possess an extremely unpleasant odor. Such compounds should have been removed completely during refining but their presence and that of free sulfur are detected by application of the *Doctor test* (ASTM D-4952, IP 30). The action on copper of any free or corrosive sulfur present in gasoline may be estimated by a procedure (ASTM D-130, ASTM D-849, IP 154) in which a strip of polished copper is immersed in the sample, which is heated under specified conditions of temperature and time, and any staining of the copper is subsequently compared with the stains on a set of reference copper strips and thus the degree of corrosivity of the test sample determined.

Total sulfur is determined by combustion in a bomb calorimeter (ASTM D-129, IP 61) and is often carried out with the determination of calorific value. The contents of the bomb are washed with distilled water into a beaker after which hydrochloric acid is added and the solution is raised to boiling point. Barium chloride is added drop by drop to the boiling solution to precipitate the sulfuric acid as granular barium sulfate. After cooling, and standing for 24 h, the precipitate is filtered off on an ashless paper, washed, ignited, and weighed as barium sulfate.

$$\%\ \text{by weight sulfur} = (\text{wt. of barium sulfate} \times 13.73)/\text{wt. of sample}$$

As an addition to the test for mercaptan sulfur by potentiometric titration (ASTM D-3227, IP 342), a piece of mechanically cleaned copper is also used to determine the amount of *corrosive sulfur* in a sample (ASTM

D-130, IP 112, IP 154, IP 411). The pure sheet copper (3.0″ × 0.5″/75 × 12 mm) is placed in a test tube with 40 ml of the sample, so that the copper is completely immersed. The tube is closed with a vented cork and heated in a boiling-water bath for 3 h. The copper strip is then compared visually with a new strip of copper for signs of tarnish. The results are recorded as:

No change:	Result negative
Slight discoloration:	Result negative
Brown shade:	Some effect
Steel gray:	Some effect
Black, not scaled:	Result positive, corrosive sulfur present
Black, scaled:	Result positive, corrosive sulfur present

Thus visual observation of the copper strip can present an indication or a conclusion of the presence or absence of corrosive sulfur. There is also a copper strip corrosion method for liquefied petroleum gases (ASTM D-1838).

5.3.5. Density (Specific Gravity)

Density (the mass of liquid per unit volume at 15°C) and the related terms *specific gravity* (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.) and *relative density* (same as *specific gravity*) are important properties of petroleum and petroleum products (Chapter 2). Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.

The determination of density (specific gravity) (ASTM D-287, ASTM D-891, ASTM D-941, ASTM D-1217, ASTM D-1298, ASTM D-1555, ASTM D-1657, ASTM D-2935, ASTM D-4052, ASTM D-5002, IP 160, IP 235, IP 365) provides a check on the uniformity of the gasoline, and it permits calculation of the weight per gallon. The temperature at which the determination is carried out and for which the calculations are to be made should also be known (ASTM D-1086). However, the methods are subject to vapor pressure constraints and are used with appropriate precautions to prevent vapor loss during sample handling and density measurement. In addition, some test methods should not be applied if the samples are so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty. The presence of such bubbles can have serious consequences for the reliability of the test data.

The current specification for automotive gasoline (ASTM D-4814) does not set limits on the density of gasoline (ASTM D 1298, IP 160). However, the density is fixed by the other chemical and physical properties of the gasoline and is important because gasoline is often bought and sold with

reference to a specific temperature, usually 15.6°C (60°F). Because the gasoline is usually not at the specified temperature, volume correction factors based on the change in density with temperature are used to correct the volume to that temperature. Volume correction factors for oxygenates differ somewhat from those for hydrocarbons, and work is in progress to determine precise correction factors for gasoline-oxygenate blends.

5.3.6. Flash Point and Fire Point

For some purposes it is necessary to have information on the initial stage of vaporization and the potential hazards that such a property can cause. To supply this need, *flash point*, *fire point*, *vapor pressure*, and evaporation/distillation methods are available.

The *flash point* is the lowest temperature at atmospheric pressure (760 mmHg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. Flash point data are used in shipping and safety regulations to define *flammable* and *combustible* materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively nonvolatile or nonflammable material. The flash point of a petroleum product is also used to detect contamination. A substantially lower flash point than expected for a product is a reliable indicator that a product has become contaminated with a more volatile product, such as gasoline. The flash point is also an aid in establishing the identity of a particular petroleum product.

Of the available test methods, the most common method of determining the flash point confines the vapor (closed cup method) until the instant the flame is applied (ASTM D-56, ASTM D-93, ASTM D-3828, 6450, IP 34, IP 94, IP 303). An alternate method that does not confine the vapor (open cup method) (ASTM D-92, ASTM D-1310, IP 36) gives slightly higher values of the flash point.

The Pensky–Marten apparatus using a closed or open system (ASTM D-93, IP 34, IP 35) is the standard instrument for flash points above 50°C (122°F), and the Abel apparatus (IP 170) is used for more volatile oils, with flash points below 50°C (122°F). The Cleveland open-cup method (ASTM D- 92, IP 36) is also used for the determination of the *fire point* (the temperature at which the sample will ignite and burn for at least 5 s).

The Pensky–Marten apparatus consists of a brass cup mounted in an air bath and heated by a gas flame. A propeller-type stirrer, operated by a flexible drive, extends from the center of the cover into the cup. The cover has four openings: one for a thermometer and the others fitted with sliding shutters for the introduction of a pilot flame and for ventilation. The tem-

perature of the oil in the cup is raised at a rate of 5–6°C/min (9–11°F/min). The stirrer is rotated at approximately 60 rpm. When the temperature has risen to approximately 15°C (27°F) from the anticipated flash point, the pilot flame is dipped into the oil vapor for 2 s for every 1°C (1.8°F) rise in temperature up to 105°C (221°F). Above 105°C (221°F), the flame is introduced for every 2°C (3.6°F) rise in temperature. The flash point is the temperature at which a distinct flash is observed when the pilot flame meets the vapor in the cup.

Erroneously high flash points can be obtained when precautions are not taken to avoid the loss of volatile material. Samples should not be stored in plastic bottles, because the volatile material may diffuse through the walls of the container. The containers should not be opened unnecessarily. The samples should not be transferred between containers unless the sample temperature is at least 20°F (11°C) below the expected flash point.

The Abel *closed-cup* apparatus (IP 170) consists of a brass cup sealed in a small water bath that is immersed in a second water bath. The cover of the brass cup is fitted in a manner similar to that in the Pensky–Marten apparatus. For crude oils and products with flash point higher than 30°C (>86°F), the outer bath is filled with water at 55°C (131°F) and is not heated further. The oil under test is then placed inside the cup. When the temperature reaches 19°C (66°F) the pilot flame is introduced every 0.5°C (1.0°F) until a flash is obtained. For oils with flash points in excess of 30°C (>86°F) and less than 50°C (<122°F), the inner water bath is filled with cold water to a depth of 35 mm. The outer bath is filled with cold water and heated at a rate of 1°C/min (1.8°F/min). The flash point is obtained as before.

From the viewpoint of safety, information about the *flash point* is of most significance at or slightly above the maximum temperatures (30–60°C, 86–140°F)) that may be encountered in storage, transportation, and use of liquid petroleum products, in either closed or open containers. In this temperature range the relative fire and explosion hazard can be estimated from the flash point. For products with flash point below 40°C (104°F) special precautions are necessary for safe handling. Flash points above 60°C (140°F) gradually lose their safety significance until they become indirect measures of some other quality.

Another test (ASTM E-659) is available that can be used as a complement to the flash point test and involves determination of the auto-ignition temperature. However, the flash point should not be confused with auto-ignition temperature that measures spontaneous combustion with no external source of ignition.

The *fire point* is the temperature to which the product must be heated under the prescribed conditions of the method to burn continuously when the mixture of vapor and air is ignited by a specified flame (ASTM D-92, IP 36).

5.3.7. Oxygenates

Blends of gasoline with oxygenates are common and, in fact, are required in certain areas. These blends consist primarily of gasoline with substantial amounts of oxygenates, which are oxygen-containing, ashless, organic compounds such as alcohols and ethers. The most common oxygenates are ethanol and methyl-*t*-butyl ether (MTBE) with lesser attention focused on ethyl-*t*-butyl ether (ETBE), *t*-amyl methyl ether (TAME), and di-*iso*-propyl ether (DIPE).

Some of the test methods originally developed for gasoline can be used for gasoline-oxygenate blends, whereas certain other test methods for gasoline are not suitable for blends. To avoid the necessity of determining in advance whether a gasoline contains oxygenates there are test methods that can be used for both gasoline and gasoline-oxygenate blends (ASTM D-4814).

In general, the test methods for determining distillation temperatures, lead content, sulfur content, copper corrosion, existent gum, and oxidation stability can be used for both gasoline and gasoline-oxygenate blends. Some of the test methods for vapor pressure and vapor-liquid ratio are sensitive to the presence of oxygenates in the gasoline and must be acknowledged accordingly.

Whereas gasoline and water are almost entirely immiscible, and will readily separate into two phases, a gasoline-oxygenate blend is used to dissolve water without phase separation. hence the use of the term *water tolerance*. Gasoline-oxygenate blends will dissolve some water but will also separate into two phases when contacted with water that is beyond the threshold concentration. Such a phenomenon is a major issue for alcohol-containing blends.

Phase separation can usually be avoided if the gasoline is sufficiently water free initially and care is taken during distribution to prevent contact with water. Gasoline-oxygenate blends can be tested for water tolerance (ASTM D-4814) by cooling gasoline under specified conditions to its expected use temperature. Formation of a haze (analogous to the cloud point; ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP 219) must be carefully distinguished from separation into two distinct phases and is not a reason for rejection of the gasoline.

5.3.8. Stability and Instability

The study of the analysis of crude oil products is incomplete without some mention of *instability* and *incompatibility*. Both result in formation and appearance of degradation products or other undesirable changes in the original properties of petroleum products.

In terms of the instability and incompatibility of petroleum and petroleum products, the unsaturated hydrocarbon content and the heteroatom content appear to represent the greatest influence. In fact, the sulfur and nitrogen content of crude oil is an important parameter in respect of the processing methods that must be used to produce gasoline of specification sulfur concentrations. There could well be a relation between nitrogen and sulfur content and crude oil (or product) stability; higher-nitrogen and—sulfur crude oils often exhibit higher sludge-forming tendencies.

Gasoline manufactured by cracking processes contains unsaturated components that may oxidize during storage and form undesirable oxidation products. Because gasoline is often stored before use, it is essential that any components should not undergo any deleterious change under storage conditions and should remain stable during their passage from the gasoline tank of a vehicle to the cylinder of its engine so that no harmful deposits are built up in the tank and gasoline lines, in the inlet system, and on the valves.

During storage, gasoline is exposed to the action of air at ambient temperature, and in its path from vehicle tank to engine it is mixed with air and also subjected to the effects of heat. An unstable gasoline will undergo oxidation and polymerization under such conditions, forming gum, a resinous material, which in the early stages of chain reaction is initiated by the formation of peroxides and catalyzed by the presence of metals, particularly copper, which may have been picked up during refining and handling operations.

Instability occurs because of a low resistance of the product to environmental (in use) influences during storage or its susceptibility to oxidative and/or other degradative processes. In case of incompatibility, degradation products form or changes occur because of an interaction of some chemical groups present in the components of the final blend.

Petroleum product components can be defined as being *incompatible* when sludge, semisolid, or solid particles (for convenience here, these are termed *secondary products* to distinguish them from the actual petroleum product) are formed during and after blending. This phenomenon usually occurs before use. If the secondary products are marginally soluble in the blended petroleum product, use might detract from the solubility of the secondary products and they will appear as sludge or sediment that can be separated by centrifuge with water (ASTM D-2709) or by extraction (ASTM D-4310, IP 53, IP 375). When the secondary products are truly insoluble, they separate and settle out as a semisolid or solid phase floating in the gasoline or are deposited on the walls and floors of containers. In addition, secondary products usually increase the viscosity of the petroleum product. Standing at low temperatures will also cause a viscosity change

(ASTM D-2532). Usually the viscosity change might be due to separation of paraffins as might occur when gasoline, but more especially diesel gasoline, is allowed to cool and stand unused overnight in low-temperature climates.

Briefly, the term *incompatibility* refers to the formation of a precipitate (or sediment) or phase separation when two liquids are mixed. The term *instability* is often used in reference to the formation of color, sediment, or gum in the liquid over a period of time. This term may be used to contrast the formation of a precipitate in the near term (almost immediately). However, the terms are often used interchangeably.

The measurement of color (ASTM D-l56, ASTM D-848, ASTM D-1209, ASTM D-1555, ASTM D-5386, IP 17) provides a rapid method of checking the degree of freedom from contamination. Observation of the test for residue on evaporation (ASTM D-381, ASTM D-1353, IP 131) provides a further guard against adventitious contamination.

Tests should also be carried out for sediment if the gasoline has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the gasoline and the resulting products. Test methods are available for the determination of sediment by extraction (ASTM D-473, IP 285) or by membrane filtration (ASTM D-4807, IP 286) and the determination of sediment simultaneously with water by centrifugation (ASTM D-96, ASTM D-1796, ASTM D-2709, ASTM D-4007, IP 373, IP 374).

Gum formation (ASTM D-525, IP 40) alludes to the formation of soluble organic material, whereas *sediment* is insoluble organic material. *Storage stability* (or *storage instability*) (ASTM D-381, ASTM D-4625, IP 131, IP 378) is a term used to describe the ability of the liquid to remain in storage over extended periods of time without appreciable deterioration as measured by gum formation and/or the formation of sediment. *Thermal stability* is defined as the ability of the liquid to withstand relatively high temperatures for short periods of time without the formation of sediment (i.e., carbonaceous deposits and/or coke). *Thermal oxidative stability* is the ability of the liquid to withstand relatively high temperatures for short periods of time in the presence of oxidation and without the formation of sediment or deterioration of properties (ASTM D-3241), and there is standard equipment for various oxidation tests (ASTM D-4871). *Stability* is also defined as the ability of the liquid to withstand long periods at temperatures up to 100°C (212°F) without degradation. Determination of the *reaction threshold temperature* for various liquid and solid materials might be beneficial (ASTM D-2883).

Existent gum is the name given to the nonvolatile residue present in the gasoline as received for test (ASTM D-381, IP 131). In this test, the sample

is evaporated from a beaker maintained at a temperature of 160–166°C (320–331°F) with the aid of a similarly heated jet of air. This material is distinguished from the *potential gum* that is obtained by aging the sample at an elevated temperature.

Thus *potential gum* is determined by the *accelerated gum test* (ASTM D-873, IP 138), which is used as a safeguard of storage stability and can be used to predict the potential for gum formation during prolonged storage. In this test, the gasoline is heated for 16 h with oxygen under pressure in a bomb at 100°C (212°F). After this time, both the gum content and the solids precipitated are measured.

Dry sludge is defined as the material separated from the bulk of an oil by filtration that is insoluble in heptane. *Existent dry sludge* is the dry sludge in the original sample as received and is distinguished from the accelerated dry sludge obtained after aging the sample by chemical addition or heat. The *existent dry sludge* is distinguished from the *potential dry sludge* that is obtained by aging the sample at an elevated temperature.

The *existent dry sludge* is operationally defined as the material separated from the bulk of a crude oil or crude oil product by filtration that is insoluble in heptane. The test is used as an indicator of process operability and as a measure of potential downstream fouling.

Attractive as they may be, any tests that involve *accelerated oxidation* of the sample must be used with caution and consideration of the chemistry. Depending on the constituents of the sample, it is quite possible that the higher temperature and extreme conditions (oxygen under pressure) may not be truly representative of the deterioration of the sample under storage conditions. The higher temperature and the oxygen under pressure might change the chemistry of the system and produce products that would not be produced under ambient storage conditions. An assessment of the composition of the gasoline before storage and application of the test will assist in this determination.

Because gasoline contains traces of nonvolatile oils and additives, the residue left in the beakers is washed with heptane before the gum residue is dried and weighed. The existent gum test (ASTM D-381, IP 131) is useful as a refinery control but is to some extent unrealistic as a criterion of performance, and therefore engine tests have been developed to determine the tendency toward inlet system deposits.

In general, gasoline instability and incompatibility can be related to the heteroatom-containing (i.e., nitrogen, oxygen, and sulfur containing) compounds. The degree of unsaturation of the gasoline (i.e., the level of olefinic species) also plays a role in determining instability/incompatibility. And recent investigations have also implicated catalytic levels of various oxidized intermediates and acids as especially deleterious for middle distillate gasoline.

5.3.9. Volatility

The volatility of a liquid is its tendency to change from the liquid to the vapor or gaseous state. Thus volatility is a primary and necessary characteristic of most liquid gasoline. The distillation profile is also a measure of the relative amounts of the gasoline constituents in petroleum.

The volatility of gasoline affects the performance of the engine in a number of ways, the chief of which are ease of starting, rate of warm-up, vapor lock, carburetor icing, and crankcase dilution (the dilution of the engine lubricating oil with the higher-boiling constituents of the gasoline). The gasoline must be sufficiently volatile to give easy starting, rapid warm-up, and adequate vaporization for proper distribution between the cylinders. Conversely, it must not be so volatile that vapor losses from the gasoline tank are excessive or that vapor is formed in the gasoline line, causing vapor lock that may impede the flow of gasoline to the carburetor.

Thus one of the most important physical parameters of gasoline is the boiling range distribution (ASTM D-86, ASTM D-1078, ASTM D-2887, ASTM D-2892, IP 123). The significance of the distillation test is the indication of volatility, which dictates the evaporation rate, an important property for gasoline used in coatings and similar applications where the premise is that the gasoline evaporates over time, leaving the coating applied to the surface. In the basic test method (ASTM D-86, IP 123) a 100-ml sample is distilled (manually or automatically) under prescribed conditions. Temperatures and volumes of condensate are recorded at regular intervals, from which the boiling profile is derived.

The determination of the boiling range distribution of gasoline by gas chromatography (ASTM D-3710) not only helps identify the constituents but also facilitates on-line controls at the refinery. This test method is designed to measure the entire boiling range of gasoline with either high or low Reid vapor pressure (ASTM D-323, IP 69). In this method, the sample is injected into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Calibration is performed with a known mixture of hydrocarbons covering the expected boiling of the sample.

Another method is described as a method for determining the carbon number distribution (ASTM D-2887, IP 321), and the data derived by this test method are essentially equivalent to that obtained by true boiling point distillation (ASTM D-2892). The sample is introduced into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the

same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution may be obtained. However, this test method is limited to samples with a boiling range greater than 55°C (100°F) and having a vapor pressure (ASTM D-323, ASTM D-4953, ASTM D-5190, ASTM D-5191, ASTM D-5482, ASTM D-6377, ASTM D-6378, IP 69, IP 394) sufficiently low to permit sampling at ambient temperature.

The volatility of petroleum and petroleum products is an important aspect of safety and quality. It would be unsafe to attempt to store highly volatile materials in the open sunlight or in an enclosed space where temperature can rise to be in excess of 37.8°C (100°F). And yet, without any indications of when the material might vaporize and spontaneously ignite, there is no way of even considering the correct storage and handling conditions.

The *boiling points* of petroleum fractions are rarely, if ever, distinct temperatures, and it is, in fact, more correct to refer to the *boiling range* of a particular fraction. To determine these ranges, the petroleum is tested in various methods of distillation, either at atmospheric pressure or at reduced pressure. A general estimate is that the limiting molecular weight range for distillation at atmospheric pressure without thermal degradation is 200–250 amu whereas the limiting molecular weight range for conventional vacuum distillation is 500–600 amu.

In each homologous series of hydrocarbons, the *boiling point* increases with molecular weight. Structure also has a marked influence, and it is a general rule that branched paraffin isomers have lower boiling points than the corresponding *n*-alkane. However, the most dramatic illustration of the variation in boiling point with carbon number is an actual plot for different hydrocarbons (Fig. 5.1). In any given series, steric effects notwithstanding, there is an increase in boiling point with an increase in carbon number of the alkyl side chain (Fig. 5-2). This particularly applies to alkyl aromatic compounds, where alkyl-substituted aromatic compounds can have higher boiling points than polycondensed aromatic systems. This fact is very meaningful when attempts are made to develop hypothetical structures for the higher-molecular-weight constituents of petroleum (Speight, 1999, 2001).

At an early stage of characterization studies, a correlation was observed between the quality of petroleum products and their hydrogen content because gasoline, kerosene, diesel gasoline, and lubricating oil are made up of hydrocarbon constituents containing high proportions of hydrogen. Thus it is not surprising that tests to determine the volatility of petroleum and petroleum products were among the first to be defined. Indeed, volatility is one of the major tests for petroleum products and it is inevitable that all products will, at some stage of their history, be tested for volatility characteristics.

The boiling range of motor gasoline falls in the range 30–210°C (86–410°F), and blending of the available refinery components can maintain balance between the different volatility requirements. The volatility of

gasoline is normally assessed by the distillation test (ASTM D-86, IP 123). Determination of the boiling range distribution of gasoline and gasoline fractions by gas chromatography (ASTM D-3710) can be used for determining the boiling point properties of oxygenate-free gasoline distillates and this test has the advantage that it uses a smaller sample size and can be more easily automated, but the data from the two tests may not be directly equivalent.

The apparatus employed for the test provides little in the way of fractionation and although the thermometer is accurately standardized at total immersion, it is used at partial immersion and no temperature corrections are made for emergent steam. However, provision is made in the test for correcting the thermometer readings for variations in atmospheric pressure whenever the barometric reading is sufficiently far from standard atmospheric pressure to make corrections desirable. Therefore, although the temperatures are highly reproducible they are not true vapor temperatures.

The *vapor pressure* of petroleum or a petroleum product is the force exerted on the walls of a closed container by the vaporized portion of a liquid. Conversely, it is the force that must be applied to the liquid to prevent it vaporizing further. The vapor pressure increases with increase in temperature and is variously expressed in terms of millimeters of mercury, pounds per square inch, or other equivalent units of pressure depending on common usage. Gasoline vapor pressure depends critically on its butane content, and in the refinery the final adjustment of vapor pressure of a gasoline to meet the specification is often made by butane injection.

The *Reid vapor pressure* (ASTM D-323, IP 69, IP 402) is a measure of the vapor pressure of petroleum or a petroleum product an oil at 37.8°C (100°F) expressed as millimeters of mercury. The apparatus used to determine the Reid vapor pressure consists of a metal cylinder, or *bomb*, fitted with an accurate dial pressure gauge or a mercury manometer. The bomb consists of two parts, an upper expansion chamber and a lower liquid chamber. The sample is cooled and poured into the lower chamber until it is full. The temperature of the air in the upper chamber is taken, and the two chambers are connected together in a gas-tight manner. The bomb is immersed upright in a water bath at 37.8°C (100°F) and shaken repeatedly until a constant pressure reading is obtained. This is corrected, from tables, for initial air temperature and pressure.

Another method (ASTM D-5191) is now most commonly referenced in gasoline regulations, and the method requires less sample and is much easier and faster to run. Other methods for determining the vapor pressure of gasoline are also available (ASTM D-4953, ASTM D-5190, ASTM D-5482).

Thus petroleum can be subdivided by distillation into a variety of fractions of different *boiling ranges* (*cut points*) with a variety of standard methods specifically designed for this task.

Distillation involves the general procedure of vaporizing the petroleum liquid in a suitable flask either at *atmospheric pressure* (ASTM D-86, ASTM D-216, ASTM D-285, ASTM D447, ASTM D-2892, ASTM D-5236, IP 24, IP 123, IP 191) or at *reduced pressure* (ASTM D-1160). Most of the methods specify an upper atmospheric equivalent temperature (AET) limit of 360°C (680°F) to mitigate the onset of thermal decomposition. For higher-boiling fractions, the spinning band distillation method and a method of distillation using a flash still are available

In the simplest case, the distillation method involves use of a standard round-bottom distillation flask of 250-ml capacity attached to a water-cooled condenser. The thermometer bulb is placed at the opening to the side arm of the flask. One hundred milliliters of sample are placed in the flask and heated by a small gas flame so as to produce ten milliliters of distillate every 4 or 5 min. The temperature of initial distillation is recorded; the temperature at which each further 10 ml distils and the final boiling point are also recorded.

Samples containing light components must be debutanized in a preliminary step. In the method, a weighed sample of 1–10 liters is distilled in a fractionating column having an efficiency at total reflux of 14–18 theoretical plates. A reflux ratio of 5:1 is maintained throughout except at the minimum pressure of 2 mmHg, where a ratio of 2:1 can be used. The mass and density of each fraction are used to prepare distillation curves either by mass or volume. This method is often referred to as the *15-5 method*.

One method (ASTM D-1160) is available to determine the boiling ranges of petroleum products to a maximum liquid temperature of 400°C (752°F) at pressures as low as 1 mmHg and is adequate for gasoline. In the method, a 200-ml sample is weighed to the nearest 0.1 g in a distillation flask. The distillation assembly is evacuated to the desired pressure, and heat is applied to the flask as rapidly as possible using a 750-W heater. When refluxing liquid appears, the rate of heating is adjusted so that the distillate is recovered at 4–8 ml/min until the distillation is complete.

Generally, the distillation tests are planned so that the data are reported in terms of one or more of the following items:

1. *Initial boiling point* is the thermometer reading in the neck of the distillation flask when the first drop of distillate leaves the tip of the condenser tube. This reading is materially affected by a number of test conditions, namely, room temperature, rate of heating, and condenser temperature.
2. *Distillation temperatures* are usually observed when the level of the distillate reaches each 10% mark on the graduated receiver, with the temperatures for the 5% and 95% marks often included. Conversely,

the volume of the distillate in the receiver, that is, the percentage recovered, is often observed at specified thermometer readings.

3. *End point* or *maximum temperature* is the highest thermometer reading observed during distillation. In most cases it is reached when all of the sample has been vaporized. If a liquid residue remains in the flask after the maximum permissible adjustments are made in heating rate, this is recorded as indicative of the presence of very-high-boiling compounds.
4. *Dry point* is the thermometer reading at the instant the flask becomes dry and is for special purposes, such as for solvents and for relatively pure hydrocarbons. For these purposes dry point is considered more indicative of the final boiling point than end point or maximum temperature.
5. *Recovery* is the total volume of distillate recovered in the graduated receiver, and *residue* is the liquid material, mostly condensed vapors, left in the flask after it has been allowed to cool at the end of distillation. The residue is measured by transferring it to an appropriate small graduated cylinder. Low or abnormally high residues indicate the absence or presence, respectively, of high-boiling components.
6. *Total recovery* is the sum of the liquid recovery and residue; *distillation loss* is determined by subtracting the total recovery from 100%. It is, of course, the measure of the portion of the vaporized sample that does not condense under the conditions of the test. Like the initial boiling point, distillation loss is affected materially by a number of test conditions, namely, condenser temperature, sampling and receiving temperatures, barometric pressure, heating rate in the early part of the distillation, and others. Provisions are made for correcting high distillation losses for the effect of low barometric pressure because of the practice of including distillation loss as one of the items in some specifications for motor gasoline.
7. *Percentage evaporated* is the percentage recovered at a specific thermometer reading or other distillation temperatures, or the converse. The amounts that have been evaporated are usually obtained by plotting observed thermometer readings against the corresponding observed recoveries plus, in each case, the distillation loss. The initial boiling point is plotted with the distillation loss as the percentage evaporated. Distillation data are reproducible, particularly for the more volatile products.

The capillary method can be used as one of two standardized methods (ASTM D-2887, ASTM D-3710) that are available for the boiling point determination of petroleum fractions and gasoline, respectively. The former

method (ASTM D-2887) utilizes nonpolar, packed gas chromatographic columns in conjunction with flame ionization detection. The upper limit of the boiling range covered by this method is approximately 540°C (1000°F) atmospheric equivalent boiling point. Recent efforts in which high-temperature gas chromatography was used have focused on extending the scope of the method for higher-boiling petroleum materials to 800°C (1470°F) atmospheric equivalent boiling point.

The measurement of pressure at the *top* of the distillation column is critical to valid distillation results because the observed vapor temperature must be corrected to the atmospheric equivalent temperature at standard pressure conditions (760 mmHg). There is a general belief that the minimum pressure should be 2 mmHg or greater for reasonably accurate measurements and correction to the atmospheric equivalent temperature. At pressures below 2 mmHg, the pressure measurement is too inaccurate and a discontinuity can arise in the atmospheric equivalent temperature distillation curve from atmospheric to vacuum distillation.

The precision and accuracy of the single internal standard method depends on the accuracy of estimating the area of the internal standard. In addition to the problems in determining the percentage of sample that elutes from a gas chromatographic column, errors can occur because the components of a sample can elute at a different time than the standards of the same boiling point.

Another aspect of volatility, namely, the tendency for gasoline to vaporize, can be expressed in terms of vapor-to-liquid ratio (V/L) at temperatures approximating those found in critical parts of the gasoline system. One standard test method (ASTM D-2533) allows the use of either of two confining fluids, glycerin or mercury. Glycerin should be used as the confining fluid only for hydrocarbon-only gasoline. Mercury must be used as the confining fluid for gasoline-oxygenate blends and can also be used for gasoline. An instrumental method that does not use a confining fluid can be used for both gasoline and gasoline-oxygenate blends (ASTM D-5188).

A linear equation method and a nomograph method can be used for estimating vapor-liquid equilibria of gasoline from vapor pressure and distillation test results (ASTM D-4814). However, these estimation methods are not applicable to gasoline-oxygenate blends.

5.3.10. Water and Sediment

However, before any volatility tests are carried out it, all water must be removed because the presence of more then 0.5% water in test samples of crude can cause several problems during distillation procedures. Water has a high heat of vaporization, necessitating the application of additional thermal energy to the distillation flask. Water is relatively easily superheated, and therefore excessive *bumping* can occur, leading to erroneous

readings, and the potential for destruction of the glass equipment is real. Steam formed during distillation can act as a carrier gas, and high-boiling point components may end up in the distillate (*steam distillation*).

Centrifugation can be used to remove water (and sediment) if the sample is not a tight emulsion. Other methods that are used to remove water include:

1. Heating in a pressure vessel to control loss of light ends,
2. Addition of calcium chloride as recommended in ASTM D-1160,
3. Addition of an azeotroping agent such as *iso*-propanol or *n*-butanol,
4. Removal of water in a preliminary low-efficiency or flash distillation followed by reblending the hydrocarbon that codistills with the water into the sample (IP 74), and
5. Separation of the water from the hydrocarbon distillate by freezing.

Water is a contaminant in gasoline and should be measured with the Karl Fischer method (ASTM E-203, ASTM D-1364, ASTM D-1744, ASTM D-4377, ASTM D-4928, ASTM D-6304), by distillation using a Dean and Stark condenser (ASTM D-4006) (Fig. 5.3), or by centrifuging (ASTM D-96) and excluded by relevant drying methods.

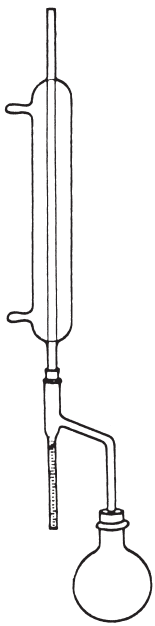

Figure 5.3. Dean and Stark adaptor on the bottom of a condenser

Tests should also be carried out for sediment if the gasoline has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the gasoline and the resulting products. Test methods are available for the determination of sediment by extraction (ASTM D-473, IP 285) or by membrane filtration (ASTM D-4807, IP 286) and the determination of simultaneously sediment with water by centrifugation (ASTM D-96, ASTM D-1796, ASTM D-2709, ASTM D-4007, IP 373, IP 374).

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CHAPTER

6

AVIATION FUEL

6.1. INTRODUCTION

The term *aviation fuel*, as used in this text, is a collective term that includes *aviation gasoline* and *aviation gas turbine fuel* as well as various types of *jet fuel* (Gruse and Stevens, 1960; Guthrie, 1967; Gottshall et al., 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Hemighaus, G. 1998; Speight, 1999; Wolveridge, 2000). Aviation fuels consist of hydrocarbons, and sulfur-containing as well as oxygen-containing impurities are limited strictly by specification. Composition specifications usually state that aviation fuel must consist entirely of hydrocarbons except for trace amounts of *approved* additives.

The two basic types of jet fuels in general use are based on kerosene (kerosene-type jet fuel) and gasoline (naphtha) (gasoline-type jet fuel). Kerosene-type jet fuel is a modified development of the illuminating kerosene originally used in gas turbine engines. Gasoline-type jet fuel has a wider boiling range and includes some gasoline fractions. In addition, a number of specialized fuel grades are required for use in high-performance military aircraft.

Kerosene-type jet fuel is medium distillate used for aviation turbine power units and usually has the same distillation characteristics and flash point as kerosene (between 150°C and 300°C but not generally above 250°C). In addition, this fuel has particular specifications (such as freezing point) that are established by the International Air Transport Association (IATA). On the other hand, aircraft gas turbine engines require a fuel with properties different from those required for aviation gasoline (ASTM D-1655). The major difference is that aircraft turbine engines require a fuel with good combustion characteristics and high energy content. However, as engine and fuel system designs have become more complicated, the fuel specifications have become more varied and restrictive.

The first aviation gas turbine engines were regarded as having noncritical fuel requirements. Ordinary illuminating kerosene was the original development fuel, but the increased complexity in design of the engine has required fuel specification tests to be more complicated and numerous.

Demands for improved performance, economy, and overhaul life will indirectly continue the trend toward additional tests.

6.2. PRODUCTION AND PROPERTIES

Aviation fuels have a narrower distillation range than motor gasoline, and the octane ratings of aviation gasoline and motor gasoline are not comparable because of the different test methods used to rate the two types of fuels. In addition, motor gasoline has a shorter storage stability lifetime than aviation gasoline and can form gum deposits that can induce poor mixture distribution and valve sticking.

Furthermore, the higher aromatics content and the possible presence of oxygenates in motor gasoline can induce solvent characteristics that are unsuitable for seals, gaskets, fuel lines, and some fuel tank materials in aircraft. Motor gasoline may also contain additives that could be incompatible with certain in-service aviation turbine fuel (ASTM D-4054, ASTM D-4307). For example, alcohols or other oxygenates can increase the tendency for the fuel to hold water, either in solution or in suspension.

Aviation gasoline, for aviation piston engines, is produced from petroleum distillation fractions containing lower-boiling hydrocarbons that are usually found in straight-run naphtha. These fractions have high contents of *iso*-pentanes and *iso*-hexane and provide needed volatility as well as high octane numbers. Higher-boiling *iso*-paraffins are provided by aviation alkylate, which consists mostly of branched octanes. Aromatics, such as benzene, toluene, and xylene, are obtained from processes such as catalytic reforming.

To increase the proportion of higher-boiling octane components, such as aviation alkylate and xylenes, the proportion of lower-boiling components must also be increased to maintain the proper volatility. *Iso*-pentane and, to some extent, *iso*-hexane are the lower-boiling components used and can be separated from naphtha by superfractionators or synthesized from the normal hydrocarbons by isomerization. In general, most aviation gasoline is made by blending a selected straight-run naphtha fraction (aviation base stock) with *iso*-pentane and aviation alkylate.

Aviation gasoline has an octane number suited to the engine, a freezing point of −60°C, and a distillation range usually within the limits of 30°C (86°F) and 180°C (356°F). Aviation gasoline specifications generally contain three main sections covering suitability, composition, and chemical and physical requirements. In addition, *gasoline type jet fuel* includes all light hydrocarbon fractions for use in aviation turbine power units and distills between 100°C (212°F) and 250°C (482°F). It is obtained by blending kerosene and gasoline or naphtha in such a way that the aromatic content

does not exceed 25% v/v and the vapor pressure is between 13.7 kPa (2 psi) and 20.6 kPa (3 psi).

Aviation turbine fuels are manufactured predominantly from straight-run kerosene or kerosene-naphtha blends in the case of wide-cut fuels that are produced from the atmospheric distillation of crude oil. Straight-run kerosene from low-sulfur (sweet) crude oil will meet all the requirements of the jet fuel specification without further refinery processing, but for the majority of feedstocks, the kerosene fraction will contain trace constituents that must be removed by hydrotreating (hydrofining) or by a chemical sweetening process (Speight, 2000).

Traditionally, *jet fuel* has been manufactured only from straight-run components, but in recent years, however, hydrocracking processes (Speight, 1999; Speight and Ozum, 2002) have been introduced that produce high-quality kerosene fractions ideal for jet fuel blending.

Because of the international nature of aviation activities, the technical requirements of all the western specifications are virtually identical, and only differences of a minor nature exist between the various specifications (ASTM D-910).

6.3. TEST METHODS

Specifications covering the various grades have been drawn up by a number of bodies, and these have been reissued from time to time as engine requirements have changed. No significant changes have now occurred in these specifications for a number of years, except for the gradual reduction in the number of grades covered.

The requirements for jet fuels stress a different combination of properties and tests than those required for aviation gasoline (ASTM D-1655). The same basic controls are needed for such properties as storage stability and corrosivity, but the gasoline antiknock tests are replaced by tests directly and indirectly controlling energy content and combustion characteristics. However, as with other petroleum products, application of sampling protocols (ASTM D-3700, ASTM D-4057, ASTM D-4177, ASTM D-4306, ASTM D-5842) is of prime importance.

6.3.1. Acidity

Acidity is a property usually found in lubricating oil (ASTM D-664, ASTM D-974, ASTM D-3339, ASTM D-5770, IP 139, IP 177, IP 431); acidic compounds can also be present in aviation turbine fuels either because of the acid treatment during the refining process or because of naturally occurring organic acids. Acidity is an undesirable property because of the pos-

sibility of metal corrosion and impairment of water separation characteristics of the fuel.

In the test method for the determination of the acidity in an aviation turbine fuel (ASTM D-3242, IP 354), a sample is dissolved in a solvent mixture (toluene plus isopropyl alcohol and a small amount of water) and under a stream of nitrogen is titrated with standard alcoholic potassium hydroxide to the color change from orange in acid to green in base via added indicator *p*-naphtholbenzein solution.

6.3.2. Additives

The various approved additives for jet fuels include oxidation inhibitors to improve storage stability, copper deactivators to neutralize the known adverse effect of copper on fuel stability, and corrosion inhibitors intended for the protection of storage tanks and pipelines. An anti-icing additive (fuel system icing inhibitor) is called for in many military fuels, and a static dissipator additive (antistatic additive) may be required to minimize fire and explosion risks due to electrostatic discharges in installations and equipment during pumping operations. Details of the various approved additives (mandatory or optional) are included in the individual specifications; moreover, the additives must be compatible with the fuel (ASTM D-4054).

Only a limited number of additives are permitted in aviation fuels, and for each fuel grade the type and concentration are closely controlled by the appropriate fuel specifications. Additives may be included for a variety of reasons, but in every case the specifications define the requirements as follows:

1. Mandatory: must be present between minimum and maximum limits.
2. Permitted: may be added up to a maximum limit.
3. Optional: may be added only within specified limits.
4. Not allowed: additives not listed in the specifications.

Although the type and amount of each additive permitted in aviation fuels are strictly limited to color dye, antioxidant, metal deactivator, corrosion inhibitor, fuel system icing inhibitor, static dissipator, and lubricity additive, test methods for checking the concentration present are not specified in every case. In some cases tests to determine the additive content (or its effect) are called for, but in other cases a written statement of its original addition (e.g., at the refinery) is accepted as adequate evidence of its presence.

After the specified amounts of color dyes have been added to aviation gasoline the color is normally only checked visually (by inspection), through

the Saybolt method (ASTM D-l56). In the past jet fuel color has also been specified by the Lovibond method (IP 17), as currently used for the color of dyed aviation gasoline, although color *by inspection* might, but not always, be considered adequate.

After the required amounts of antioxidant, metal deactivator, or corrosion inhibitor have been added to aviation fuels it is not normal to carry out any checks on the concentrations, and no test methods are included in specifications for this purpose. Occasionally a need arises to determine the amount of corrosion inhibitor remaining in a fuel, and several analytical methods have been developed, none of which has yet been standardized.

Fuel system icing inhibitor (FSII) used in jet fuels can be lost by evaporation and is also lost rapidly into any water that may contact the fuel during transportation. Routine checks must therefore be made on the icing inhibitor content of the fuel, right up to the point of delivery to aircraft in some instances (IP 277), but for routine test purposes a simpler colorimetric version of this test is commonly used.

Many fuel specifications require the use of static dissipator additive to improve safety in fuel handling. In such cases the specification defines both minimum and maximum electrical conductivity; the minimum level ensures adequate charge relaxation whereas the maximum prevents too high a conductivity, because this can upset some capacitance-type fuel gauges in aircraft (ASTM D-2624, ASTM D-4308, IP 274). The standard test methods (ASTM D-2624, IP 274) employ an immersible conductivity cell and field meter intended for measuring the conductivity of fuel in storage tanks.

As a valuable step toward rationalizing the approval procedure for aviation fuel additives, guidelines are available (ASTM D-1655, ASTM D-4054). Tests are available for measuring or specifying additives such as color dyes (ASTM D-156, ASTM D-2392, ASTM D-5386, IP 17), corrosion inhibitors (often measured by the corrosivity of the fuel—ASTM D-130, ASTM D-5968, IP 154), lubricity (ASTM D-5001), fuel system icing inhibitors (ASTM D-910, ASTM D-4171, ASTM D-5006, IP 277), and static dissipator additives (ASTM D-2624, ASTM D-4865, IP 274).

6.3.3. Calorific Value (Heat of Combustion)

The heat of combustion (ASTM D-240, ASTM D-1405, ASTM D-2382, ASTM D-3338, ASTM D-4529, ASTM D-4809, ASTM D-6446, IP 12) is a direct measure of fuel energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter. This fuel property affects the economics of engine performance, and the specified minimum value is a compromise between the conflicting requirements of maximum fuel availability and good fuel consumption characteristics.

As a general guideline, the heat of combustion is on the order of 18,000–21,000 Btu/lb (10,000–11,600 cal/g) for petroleum, on the order of 20,000–20,700 Btu/lb (11,100–11,500 cal/g) for gasoline, on the order of 19,000–20,200 Btu/lb (10,500–1,200 cal/g) for kerosene and similar fuels, and on the order of 17,300–20,200 Btu/lb (9,600–11,200 cal/gm) for fuel oil.

When an experimental determination of heat of combustion is not available and cannot be made conveniently, an estimate might be considered satisfactory (ASTM D-6446). In this test method, the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the hydrogen content (ASTM D-1217, ASTM D-1298, ASTM D-3701, ASTM D-4052, ASTM D-4808, ASTM D-5291 IP 160, IP 365), density (ASTM D-129, ASTM D-1250, ASTM D-1266, ASTM D-2622, ASTM D-3120, IP 61, IP 107), and sulfur content (ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 336, IP 373) of the sample are determined by experimental test methods and the net heat of combustion is calculated using the values obtained by these test methods based on reported correlations.

A simple equation for calculating the heat of combustion is:

$$Q = 12{,}400 - 2{,}100d^2$$

where Q is the heat of combustion and d is the specific gravity. However, the accuracy of any method used to calculate such a property is not guaranteed, and the result can only be used as a guide to or approximation of the measured value.

An alternative criterion of energy content is the *aniline gravity product* (AGP), which is related to calorific value (ASTM D-1405, IP 193). The aniline gravity product is the product of the API gravity (ASTM D-287, ASTM D-1298) and the aniline point of the fuel (ASTM D-611, IP 2). The aniline point is the lowest temperature at which the fuel is miscible with an equal volume of aniline and is inversely proportional to the aromatic content. The relationship between the aniline gravity product and calorific value is given in the method. In another method (ASTM D-3338), the heat of combustion is calculated from the fuel density, the 10%, 50%, and 90% distillation temperatures, and the aromatic content. However, neither method is legally acceptable, and other methods (ASTM D-240, ASTM D-1655, ASTM D-4809) are preferred.

Jet fuels of the same class can vary widely in their burning quality as measured by carbon deposition, smoke formation, and flame radiation. This is a function of hydrocarbon composition—paraffins have excellent burning

properties, in contrast to those of the aromatics (particularly the polynuclear aromatic hydrocarbons). As a control measure the smoke point test (ASTM D-l322, IP 57) gives the maximum smokeless flame height in millimeters at which the fuel will burn in a wick-fed lamp under prescribed conditions. The combustion performance of wide-cut fuels correlates well with smoke point when a fuel volatility factor is included, because carbon formation tends to increase with boiling point. A minimum smoke volatility index (SVI) value is specified and is defined as:

$$\text{SVI} = \text{smoke point} + 0.42\ (\text{percent distilled below } 204°\text{C}/400°\text{F}).$$

However, the smoke point is not always a reliable criterion of combustion performance and should be used in conjunction with other properties. Various alternative laboratory test methods have previously been specified such as the lamp burning test (ASTM D-187, IP 10) and a limit on the polynuclear aromatic content (ASTM D-1840), as well as the luminometer number (ASTM D-l740).

The test for luminometer number (ASTM D-l740) was developed because certain designs of jet engine have the potential for a shortened combustion chamber life because of high liner temperatures caused by radiant heat from luminous flames. The test apparatus is a smoke point lamp modified to include a photoelectric cell for flame radiation measurement and a thermocouple to measure temperature rise across the flame. The fuel luminometer number (LN) is expressed on an arbitrary scale on which values of 0 to 100 are given to the reference fuels tetralin and *iso*-octane, respectively.

6.3.4. Composition

The first level of compositional information is group-type totals as deduced by adsorption chromatography (ASTM D-1319, IP 156). This method is applied to data related to the volume percent saturates, olefins, and aromatics in materials that boil below 315°C (600°F). This temperature range includes jet fuels (but not all diesel fuel), most of which have an end point above 315°C.

Aviation gasoline consists substantially of hydrocarbons; sulfur-containing and oxygen-containing impurities are strictly limited by specification, and only certain additives are permitted. Straight-run gasoline from crude oil, containing varying proportions of paraffins, naphthenes, and aromatics, invariably lacks the high proportion of branch chain paraffins (*iso*-paraffins) required to produce the higher-quality aviation fuels.

Unsaturated hydrocarbons (olefins) are relatively unstable and give rise to excessive gum formation. Only the lower grades of fuel can include a

proportion of straight-run gasoline, and the higher grades consist mainly of *iso*-paraffins with a small amount of aromatic material to improve the rich mixture antiknock performance. The main component of these high-grade fuels is *iso*-octane produced in the alkylation process by reaction of refinery butenes with *iso*-butane over the acid catalysts. To meet the volatility requirements of the final blend, there is added a small proportion of *iso*-pentane, obtained by superfractionation of light straight-run gasoline. The aromatic component required to improve rich mixture rating is now usually a catalytic reformate, and the amount added is indirectly limited by the gravimetric calorific value requirement.

Jet fuels consist entirely of hydrocarbons except for trace quantities of sulfur compounds and approved additives. Jet fuels are produced, for example, by blending straight-run distillate components, and olefins are limited by specification (ASTM D-l319, IP 156) or by the bromine number (ASTM D-1159, ASTM D-2710, IP 130).

The bromine number is the number of grams of bromine that will react with 100 g of the sample under the test conditions. The magnitude of bromine number is an indication of the quantity of bromine-reactive constituents and is not an identification of constituents. It is used as a measure of aliphatic unsaturation in petroleum samples and percentage of olefins in petroleum distillates boiling up to approximately 315°C (600°F). In the test, a known weight of the sample dissolved in a specified solvent maintained at 0–5°C (32–41°F) is titrated with standard bromide-bromate solution. Determination of the end point is method dependent.

Because the aromatic hydrocarbon content of aviation turbine fuels affects their combustion characteristics and smoke forming tendencies, the amounts of aromatics (ASTM D-1319, IP 156) are limited. Aromatic constituents also increase the luminosity of the combustion flame (ASTM D-l740), which can adversely affect the life of the combustion chamber.

The aromatics content of aviation turbine fuel is included in the aviation turbine fuel specification (ASTM D-1655). Another test method for aromatics content (ASTM D-5186) involves the injection of a small aliquot of the fuel sample onto a packed silica adsorption column and elution with supercritical carbon dioxide as the mobile phase. Mono- and polynuclear aromatics in the sample are separated from nonaromatics and detected with a flame ionization detector. The chromatographic areas corresponding to the mono- and polynuclear and nonaromatic components are determined, and the mass percent content of each of these groups is calculated by area normalization. The results obtained by this method are at least statistically more precise than those obtained by other test methods (ASTM D-1319, ASTM D-2425).

Although the boiling range of aviation gasoline will differ from that of automobile gasoline, many of the tests designated for automotive gasoline

(Chapter 5) can also be applied to the determination of the aromatic constituents of aviation gasoline (ASTM D-86, ASTM D-1319, ASTM D-4420, ASTM D-5443, ASTM D-5580, ASTM D-5769, ASTM D-5986, IP 123 IP 156).

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined by low-resolution magnetic resonance spectroscopy (ASTM D-3701, ASTM D-4808) and by high-resolution nuclear magnetic resonance spectroscopy (ASTM D-5292). The data produced by magnetic resonance spectroscopic methods are not equivalent to mass- or volume-percent aromatics determinations by the chromatographic methods because these methods determine the mass- or volume-percentage of molecules that have one or more aromatic rings. Chromatographic methods can also include alkyl side chains (on aromatic rings) within the aromatics fraction. Naphthalene content is an important quality parameter of jet fuel and is determined by ultraviolet spectrophotometry (ASTM D-1840).

As with other fuels, heteroatoms, mainly sulfur and nitrogen compounds, cannot be ignored, and well-established methods are available for determining the concentration of these elements. The combination of gas chromatography with element-selective detection gives information about the distribution of the element. In addition, many individual heteroatomic compounds can be determined.

The principal non-hydrocarbon components are sulfur compounds that vary with the source of the crude oil. The sulfur content of a feedstock or fuel is determined by burning a sample of the fuel and determining the amount of sulfur oxides that are formed (ASTM D-l26, IP 107). Generally, current desulfurization technologies are capable of reducing sulfur to the desired levels (ASTM D-1266, ASTM D-1552, ASTM D-2622, ASTM D-4294, IP 107). High levels of sulfur compounds adversely affect the fuel performance in the combustion chamber, and the presence of large amounts of oxides of sulfur in the combustion gases is undesirable because of possible corrosion.

Some sulfur compounds can also have a corroding action on the various metals of the engine system, varying according to the chemical type of sulfur compound present. Fuel corrosivity is assessed by its action on copper and is controlled by the copper strip test (ASTM D-130, IP 154), which specifies that not more than a slight stain shall be observed when the polished strip is immersed in fuel heated for 2 h in a bomb at 100°C (212°F). This particular method is not always capable of reflecting fuel corrosivity toward other fuel system metals. For example, service experience with corrosion of silver components in certain engine fuel systems led to the development of a silver corrosion test (IP 227). The mercaptan sulfur content (ASTM D-1219, ASTM D-3227, IP 104, IP 342) of jet fuels is limited because of objectionable odor, adverse effect on certain fuel system elastomers, and

corrosiveness toward fuel system metals. As an alternative to determining the mercaptan content, a negative result by the Doctor test (ASTM D-484, ASTM D-4952, IP 30) is usually acceptable.

Oxygenated constituents present as acidic compounds such as phenols and naphthenic acids are controlled in different specifications by a variety of acidity tests. The total acidity (ASTM D-974, IP 139, IP 273) is still widely used but has been found to be insufficiently sensitive to detect trace acidic materials that can adversely affect the water-separating properties of fuel. Oxygen-containing impurities in the form of gum are limited by the existent gum method (ASTM D-381, IP 131) and potential gum method (ASTM D-873, IP 138). With respect to aviation turbine fuels, large quantities of gum are indicative of contamination of fuel by higher-boiling oils (ASTM D-86, IP 123) or by particulate matter (ASTM D-2276, ASTM D-5452, ASTM D-6217, IP 216, IP 415). In the existent gum test for aviation fuel, a measured quantity of fuel is evaporated under controlled conditions of temperature and flow of air or steam. The residue is weighed and reported.

Control of dirt and other particles involves use of a membrane filtration method (ASTM D-2276, IP 216) in which the dirt retained by filtration of a sample through a cellulose membrane is expressed as weight per unit volume of the fuel. This test provides field quality control of dirt content and can be supplemented by a visual assessment of membrane appearance after test against color standards (ASTM D-3830). However, no direct relationship exists between particulate content weight and membrane color, and field experience is required to assess the results by either method.

Jet fuel is tested for being *clear and bright* by visual examination of a sample (ASTM D-4176).

Another contamination problem is that of microbiological growth activity, which can give rise to service troubles of various types. This problem can generally be avoided by the adoption of good housekeeping techniques by all concerned, but major incidents in recent years have led to the development of several microbiological monitoring tests for aviation fuel. In one of these tests, fuel is filtered through a sterile membrane that is subsequently cultured for microbiological growths; other tests use various techniques to detect the presence of viable microbiological matter, but none of the tests has yet been standardized.

Correlative methods are also available for application to aviation fuels. Such methods include the use of viscosity-temperature charts (ASTM D-341), calculation of the cetane index (ASTM D-976, ASTM D-4737), calculation of the viscosity index (ASTM D-2270), calculation of the viscosity gravity constant (ASTM D-2501), calculation of the true vapor pressure (ASTM D-2889), and estimation of the heat of combustion (ASTM D-3338).

6.3.5. Density (Specific Gravity)

The density (specific gravity) of a fuel is a measure of the mass per unit volume and can be determined directly with calibrated glass hydrometers (Chapters 4 and 5).

Density (specific gravity) (ASTM D-1298, IP 160) is an important property of aviation fuel as an indicator of the total energy content of a fuel uplift on a weight and/or volume basis. Variation in density is controlled within broad limits to ensure engine control. Both fuel specific gravity and calorific value vary somewhat according to crude source, paraffinic fuels having a slightly lower specific gravity but higher gravimetric calorific value than those from naphthenic crude oils.

Density is used in fuel load calculations, because weight or volume fuel limitations (or both) may be necessary according to the type of aircraft and flight pattern involved. In most cases the volume of fuel that can be carried is limited by tank capacity, and to achieve maximum range a high-density fuel is preferred because this will provide the greatest heating value per gallon (liter) of fuel. The calorific (heating) value per unit weight in kg) of fuel decreases with increasing density, and when the weight of fuel that can be carried is limited it may be advantageous to use a lower-density fuel, provided adequate tank capacity is available.

In the U.S. it is more common to specify fuel density in terms of the API gravity (ASTM D-287):

$$\text{API gravity, degrees} = [141.5/(\text{specific gravity } 60°/60°\text{F})] - 131.5$$

Aviation fuel might be expected to have an API gravity in the range of 57 to 35 (specific gravity: 0.75 to 0.85, respectively).

6.3.6. Flash Point

The flash point test is a guide to the fire hazard associated with the use of the fuel; the flash point can be determined by several test methods, and the results are not always strictly comparable.

The minimum flash point is usually defined by the Abel method (IP 170), except for high-flash kerosene, where the Pensky–Martens method (ASTM D-93, IP 34) is specified. The TAG method (ASTM D-56) is used for both the minimum and maximum limits, whereas certain military specifications also give minimum limits by the Pensky–Martens method (ASTM D-93, IP 34). The Abel method (IP 170) can give results up to 2–3°C (3–5°F) lower than the TAG method (ASTM D-56).

Similarly, for jet fuel the flash point is a guide to the fire hazard associated with the fuel and can be determined by the same test methods as noted

above (ASTM D-56, ASTM D-93, ASTM D-3828, IP 34, IP 170, IP 303), except for high-flash kerosene, where the method (ASTM D-93, IP 34) is specified.

It should be noted that the various flash point methods can yield different numerical results, and in the case of the two most commonly used methods (Abel and TAG) it has been found that the former (IP 170) can give results up to 1–2°C lower than the latter method (ASTM D-56). Setaflash (ASTM D-3828/ IP 303) results are generally very close to Abel values.

6.3.7. Freezing Point

The freezing point of aviation fuel is an index of the lowest temperature of its utility for the specified applications. Aviation fuels must have acceptable freezing point and low-temperature pumpability characteristics so that adequate fuel flow to the engine is maintained at high altitude; this is a requirement of aviation specifications. (ASTM D-910, ASTM D-1655). Maximum freezing point values are specified for all types of aviation fuel as a guide to the lowest temperature at which the fuel can be used without risk of the separation of solid hydrocarbons. The solidified hydrocarbons could lead to clogging of fuel lines or fuel filters and loss in available fuel load due to retention of solidified fuel in the tanks. The freezing point of the fuel (typically in the range –40 to –65°C, –40 to –85°F) must always be lower than the minimum operational fuel temperature. The freezing point specification is retained as a specification property to predict and safeguard high-altitude performance

Three test methods are available for determination of the freezing point. All three methods have been found to give equivalent results. However, when a specification calls for a specific test, only that test must be used.

In the first test (ASTM D-2386, IP 16), a measured fuel sample is placed in a jacketed sample tube also holding a thermometer and a stirrer. The tube is placed in a vacuum flask containing the cooling medium. Various coolants used are acetone, methyl alcohol, ethyl alcohol, or isopropyl alcohol, solid carbon dioxide, or liquid nitrogen. As the sample cools, it is continuously stirred. The temperature at which the hydrocarbon crystals appear is recorded. The jacketed sample is removed from the coolant and allowed to warm, under continuous stirring. The temperature at which the crystals completely disappear is recorded.

In the second test (ASTM D-5901, IP 434), an automated optical method is used for the temperature range to –70°C (–94°F). In this method, a 25-min portion of the fuel is placed in a test chamber that is cooled while continuously being stirred and monitored by an optical system. The temperature of the specimen is measured with an electronic measuring

device, and the temperatures when crystals first appear and then, on warming, disappear are recorded.

In the third method (ASTM D-5972, IP 435), an automated phase transition method is used in the temperature range –80 to 20°C (–112°F to 68°F). In this test, a specimen is cooled at a rate of 15 ± 5°C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an array of optical detectors for the first formation of solid hydrocarbon crystals. After that the specimen is warmed at the rate of 10 ± 0.5°C/min until all crystals return to the liquid phase, and that temperature is also recorded.

An alternative method of defining the low-temperature pumpability limits of jet fuel, the cold flow test (IP 217), is also available but may not give an adequate safety margin for the behavior of the fuel in service.

6.3.8. Knock and Antiknock Properties

The various fuel grades are classified by their *antiknock* quality characteristics as determined in single-cylinder laboratory engines. Knock, or detonation, in an engine is a form of abnormal combustion where the air/fuel charge in the cylinder ignites spontaneously in a localized area instead of being consumed progressively by the spark-initiated flame front. Such knocking combustion can damage the engine and give serious power loss if allowed to persist, and the various grades are designed to guarantee knock-free operation for a range of engines from those used in light aircraft up to high-powered transport and military types.

The antiknock ratings of aviation gasoline are determined in standard laboratory engines by matching their performance against reference blends of pure *iso*-octane and *n*-heptane. Fuel rating is expressed as an octane number (ON), which is defined as the percentage of *iso*-octane in the matching reference blend. Fuels of higher performance than *iso*-octane (100 ON) are tested against blends of *iso*-octane with various amounts of antiknock additive. The rating of such fuel is expressed as a performance number (PN), defined as the maximum knock-free power output obtained from the fuel expressed as a percentage of the power obtainable on *iso*-octane.

The antiknock rating of fuel varies according to the air-fuel mixture strength used, and this fact is used in defining the performance requirements of the higher-grade aviation fuels. As mixture strength is increased (richened), the additional fuel acts as an internal coolant and suppresses knocking combustion, thus permitting a higher power rating to be obtained. Because maximum power output is the prime requirement of an engine under rich takeoff conditions, the *rich mixture performance* of a fuel is determined in a special supercharged single-cylinder engine (ASTM D-909,

IP 119); *weak mixture performance* is also determined (ASTM D 2700, IP 236).

The higher grades of fuel are thus classified by their specified antiknock ratings under both sets of test conditions. For example, 100/130 grade fuel has an antiknock quality of 100 minimum by the weak mixture test procedure and 130 minimum by the rich mixture procedure. Octane numbers are used to specify ratings of 100 and below, whereas performance numbers are used above 100.

6.3.9. Pour Point

The *pour point* of a petroleum product is an index of the lowest temperature at which the product will flow under specified conditions. Pour point data can be used to supplement other measurements of cold flow behavior (such as the freezing point).

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 characteristics. 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, a petroleum product that contains wax produces an irregular flow behavior when the wax begins to separate. This type of product petroleum possesses viscosity relationships that are difficult to predict in operating conditions. This complex behavior may limit the value of pour point data, but laboratory pumpability tests (ASTM D-3245, IP 230) are available that, with the freezing point (ASTM D-2386, ASTM D-5901, ASTM D-5972, IP 16, IP 434, IP 435), give an estimate of minimum handling temperature and minimum line or storage temperature.

6.3.10. Storage Stability

Aviation fuel must retain its required properties for long periods of storage in all kinds of climates. Unstable fuels oxidize and form oxidation products that remain as a resinous solid or *gum* on induction manifolds, carburetors, and valves as the fuel is evaporated. Hence, there is a limitation of olefins in the fuel; they are extremely reactive and form resinous products readily.

Thus formation of this undesirable gum is strictly limited and is assessed by the existent and accelerated (or potential) gum tests.

The existent gum value (ASTM D-381, IP 131) is the gum actually present in the fuel at the time of test and is measured as the weight of residue obtained after controlled evaporation of a standard volume of fuel. The accelerated gum test (ASTM D-873, IP 138) is a safeguard of storage stability and predicts the possibility of gum forming during protracted storage and decomposition of the antiknock additive. In this test, the fuel is heated for 16 h with oxygen under pressure in a bomb at 100°C (212°F) and then both the gum content and amount of precipitate are measured.

Another test used for determining the extent of oxidation of aviation fuels is the determination of the hydroperoxide number (ASTM D-6447) and the peroxide number (ASTM D-3703). Deterioration of aviation fuel results in the formation of the peroxides as well as other oxygen-containing compounds ,and these numbers are indications of the quantity of oxidizing constituents present in the sample as determined by measurement of the compounds that will oxidize potassium iodide.

The determination of hydroperoxide number is significant because of the adverse effect of hydroperoxides on certain elastomers in the fuel systems. This method (ASTM D-6447) measures the same peroxide species, primarily the hydroperoxides in aviation fuels. This test method does not use the ozone-depleting substance 1,1,2-trichloro-1,2,2-trifluoroethane (ASTM D-3703) and is applicable to any water-insoluble, organic fluid, particularly diesel fuels, gasoline, and kerosene. In this method, a quantity of sample is contacted with aqueous potassium iodide (KI) solution in the presence of acid. The hydroperoxides present are reduced by potassium iodide, liberating an equivalent amount of iodine, which is quantified by voltametric analysis.

The determination of peroxide number of aviation turbine fuel is important because of the adverse effects of peroxides on certain elastomers in the fuel system. In the test, the sample is dissolved (unlike ASTM D-6447) in 1,1,2-trichloro-l,2,2-trifluoroethane and is contacted within an aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide, whereupon an equivalent amount of iodine is released that is titrated with standard sodium thiosulfate solution and a starch indicator.

Other tests for storage stability include determination of color formation and sediment (ASTM D-4625, ASTM D-5304) in which reactivity to oxygen at high temperatures is determined by the amount of sediment formation as well as any color changes.

6.3.11. Thermal Stability

Although the conventional (storage) stability of aviation fuel has long been defined and controlled by the existent and accelerated gum tests, another

test is required to measure the stability of a fuel to the thermal stresses that can arise during sustained supersonic flight and in some high-subsonic applications.

In high-speed flight, the fuel is subjected to considerable heat input due to kinetic heating of the airframe and also to the use of the bulk fuel as a coolant for engine oil, hydraulic and air conditioning equipment, etc. Consequently, fuel for supersonic flight must perform satisfactorily at temperatures up to about 250°C (480°F) without formation of lacquer and deposits that can adversely affect the efficiency of heat exchangers, metering devices, fuel filters, and injector nozzles. The initial problem was that of reduced overhaul life in military engines due to high fuel system temperatures upstream of the injector nozzles, giving rise to deposit formation.

Hence the application of the fuel coker test (ASTM D-l660, IP 197) for assessing the tendency of jet fuels to deposit thermal decomposition products in fuel systems. In this test, fuel is pumped through a preheater tube assembly representing fuel/oil heat exchange systems and then through a sintered stainless steel filter representing nozzles and fine orifices where fuel degradation products could become trapped. Fuel degradation is determined by pressure drop across the filter as well as by visual preheater tube deposit condition and is rated numerically by application of the various color standard tests (ASTM D-l56, ASTM D-848, ASTM D-1209, ASTM D-1555, ASTM D-5386, IP 17).

The fuel coker test suffers from precision problems and has been largely replaced by a test for the thermal oxidation stability of the fuel (ASTM D-3241, IP 323) that overcomes the disadvantages of the fuel coker test in fuel specifications.

6.3.12. Viscosity

Viscosity can significantly affect the lubricating property of the fuel and can have an influence on fuel pump service life.

The viscosity (ASTM D-445, IP 71) of fuels at low temperature is limited to ensure that adequate fuel flow and pressure are maintained under all operating conditions and that fuel injection nozzles and system controls will operate down to design temperature conditions.

6.3.13. Volatility

Fuels must be easily convertible from storage in the liquid form to the vapor phase in the engine to allow formation of the combustible air-fuel vapor mixture. If gasoline fuel volatility were too low, liquid fuel would enter the cylinder and wash lubricating oil from the walls and pistons and so lead to increased engine wear; a further effect would be to cause dilution of the

crankcase oil; poor volatility can also give rise to poor distribution of mixture strength between cylinders. Conversely, if volatility is too high, the fuel can vaporize in the fuel tank and supply lines, giving undue venting losses and the possibility of fuel starvation through *vapor lock* in the fuel lines. The cooling effect due to rapid vaporization of excessive amounts of highly volatile materials can also cause ice formation in the carburetor under certain conditions of humidity and air temperature.

One of the most important physical parameters defining these products is their boiling range distribution (ASTM D-86, ASTM D-1078, ASTM D-2887, ASTM D-2892, IP 123). However, this method is a low-efficiency, one-theoretical plate distillation, and, although it has been adequate for product specification purposes, true boiling point (TBP) data are also required (ASTM D-2887, ASTM D-2892).

In the simplest test method (ASTM D-86, IP 123) a 100-ml sample is distilled (manually or automatically) under prescribed conditions. Temperatures and volumes of condensate are recorded at regular intervals from which the boiling profile is derived. Distillation points of 10%, 20%, 50%, and 90% are specified in various ways to ensure that a properly balanced fuel is produced with no undue proportion of light or heavy fractions. The distillation end point excludes any heavy material that would give poor fuel vaporization and ultimately affect engine combustion performance.

The determination of the boiling range distribution of aviation fuel by gas chromatography (ASTM D-2887, ASTM D-3710) not only helps identify the constituents but also facilitates on-line controls at the refinery. This test method is designed to measure the entire boiling range of the fuel that has either high or low Reid vapor pressure (ASTM D-323, IP 69). In either method, the sample is injected into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Calibration is performed with a known mixture of hydrocarbons covering the expected boiling range of the sample.

Another method is described as a method for determining the carbon number distribution (ASTM D-2887, IP 321), and the data derived by this test method are essentially equivalent to that obtained by true boiling point (TBP) distillation (ASTM D-2892). The sample is introduced into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution may be obtained. However, this test method is limited to samples having a boiling range greater than 55°C (100°F) and having a

vapor pressure (ASTM D-323, ASTM D-4953, ASTM D-5190, ASTM D-5191, ASTM D-5482, ASTM D-6377, ASTM D-6378, IP 69, IP 394) sufficiently low to permit sampling at ambient temperature.

6.3.14. Water

Because of their higher density and viscosity, jet fuels tend to retain fine particulate matter and water droplets in suspension for a much longer time than aviation gasoline.

Jet fuels can also vary considerably in their tendency to pick up and retain water droplets or to hold fine water hazes in suspension depending on the presence of trace surface-active impurities (surfactants). Some of these materials (such as sulfonic and naphthenic acids and their sodium salts) may originate from the crude source or from certain refinery treating processes, whereas others may be picked up by contact with other products during transportation to the airfield, particularly in multiproduct pipelines. These latter materials may be natural contaminants from other less highly refined products (e.g., burning oils) or may consist of additives from motor gasoline (such as glycol type anti-icing agents). It should be noted that some of the additives specified for jet fuel use (e.g., corrosion inhibitors and static dissipator additive) also have surface-active properties.

The presence of surfactants can also impair the performance of the water-separating equipment (filter/separators) widely used throughout fuel handling systems to remove the traces of free (undissolved) water, particularly at the later stages before delivery to aircraft. Very small traces of free water can adversely affect jet engine and aircraft operations in several ways, and the water retention and separating properties of jet fuels have become a critical quality consideration in recent years.

Free water in jet fuels can be detected by the use of the Karl Fischer titration method (ASTM D-1744) or by observing color changes when chemicals go into aqueous solution (ASTM D-3240). The standard water reaction test for jet fuel (ASTM D-1094, IP 289) is the same as for aviation gasoline, but the interface and separation ratings are more critically defined. Test assessment is by subjective visual observation and, although quite precise when made by an experienced operator, the test can cause rating difficulties under borderline conditions. As a consequence, a more objective test, known as the water separometer test, is now included in many specifications (ASTM D-2550).

In this test, fuel is mechanically mixed with a small quantity of water and the resulting emulsion is passed through a miniature water coalescing pad and then through a settling chamber followed by a photoelectric device that measures the clarity of the effluent fuel. A good fuel, which has easily shed the entrained water, has a high rating of water separometer index-modified

(WSIM) on a numerical scale directly related to the percentage of light transmission.

There is also a *water reaction test* that is used to estimate, and prevent, the addition of high-octane, water-soluble components such as ethyl alcohol to aviation gasoline. The test method involves shaking 80 ml of fuel with 20 ml of water under standard conditions and observing phase volume changes and interface condition.

It is specified that phase volume change shall not exceed 2 ml and that the interface shall be substantially free from bubbles or scum, with sharp separation of the phases without emulsion or precipitate within or upon either layer. The long-established standard test methods for water reaction (ASTM D-1094, ASTM D-3948, IP 2896) cover the volume change and the interface condition, and special clauses have been included in most specifications to cover the phase separation requirements.

In addition to appreciable amounts of water (ASTM D-4176, ASTM D-4860), sediment can also occur and will cause fouling of the fuel handling facilities and the fuel system. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank to the combustor. A test method is available to determine the water and sediment in fuels (ASTM D-2709). In this test, a sample of fuel is centrifuged at a rcf of 800 for 10 min at 21–32°C in a centrifuge tube readable to 0.005 ml and measurable to 0.01 ml. After centrifugation, the volume of water and sediment that has settled into the tip of the centrifuge tube is read to the nearest 0.005 ml.

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CHAPTER

7

KEROSENE

7.1. INTRODUCTION

Kerosene (*kerosine*), also called paraffin or paraffin oil, is a flammable pale yellow or colorless oily liquid with a characteristic odor intermediate in volatility between gasoline and gas/diesel oil that distills between 125°C (257°F) and 260°C (500°F) (Table 7.1; Fig. 7.1) (Gruse and Stevens, 1960; Guthrie, 1967; Sefton, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin 1984; Chenier, 1992; Hoffman and McKetta, 1993; Hemighaus, G. 1998; Speight, 1999; Heinrich and Duée, 2000).

Kerosene is a refined petroleum distillate that has a flash point about 25°C (77°F) and is suitable for use as an illuminant when burned in a wide lamp. The term *kerosene* is also too often incorrectly applied to various fuel oils, but a fuel oil is actually any liquid or liquid petroleum product that produces heat when burned in a suitable container or that produces power when burned in an engine.

In the early years of the petroleum industry kerosene was its largest-selling and most important product. The demand was such that many refiners, using a variety of crude oils, made as wide a distillation cut as possible to increase its availability, thereby causing the product to have a dangerously low flash point and to include undesirable higher-boiling fractions. Burning oils are currently manufactured from carefully selected crude oils or by the use of special refining procedures, to give products of the requisite volatility and high burning quality.

7.2. PRODUCTION AND PROPERTIES

Kerosene was first manufactured in the 1850s from coal tar, hence the name *coal oil* as often applied to kerosene, but petroleum became the major source after 1859. From that time, the kerosene fraction was, and has remained, a distillation fraction of petroleum. However, the quantity and quality vary with the type of crude oil, and although some crude oils yield excellent kerosene quite simply, others produce kerosene that requires substantial refining.

Table 7.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

Kerosene is less volatile than gasoline (boiling range approximately 140°C/285°F to 320°C/610°F) and is obtained by fractional distillation of petroleum (Speight, 1999). To decrease smoke generation, paraffinic stocks are used normally in the manufacture of kerosene for lighting and heating. For the same reason, aromatic stocks and cracked components are avoided. Some crude oils, especially the paraffinic crude oils, contain kerosene fractions of very high quality, but other crude oils, such as those having an asphalt base, must be thoroughly refined to remove aromatics and sulfur compounds before a satisfactory kerosene fraction can be obtained. Cracking the less volatile constituents of petroleum is now a major process for kerosene production.

In the early days, the poorer-quality kerosene was treated with large quantities of sulfuric acid to convert it into marketable products. However, this treatment resulted in high acid and kerosene losses, but the later development of the Edeleanu process (Speight, 1999) overcame these problems. Kerosene is a very stable product, and additives are not required to improve the quality. Apart from the removal of excessive quantities of aromatics by the Edeleanu process, kerosene fractions may need only a lye wash or a Doctor treatment if hydrogen sulfide is present to remove mercaptans (Speight, 1999). When low-sulfur paraffinic crude oil is fractionated to yield the proper boiling range fraction, only a drying operation may be required before shipment.

Kerosene from naphthenic oil or high-sulfur crude oil requires hydrotreating, acid treatment and water wash, or extraction with a solvent and caustic wash and clay brightening to remove undesirable aromatics or

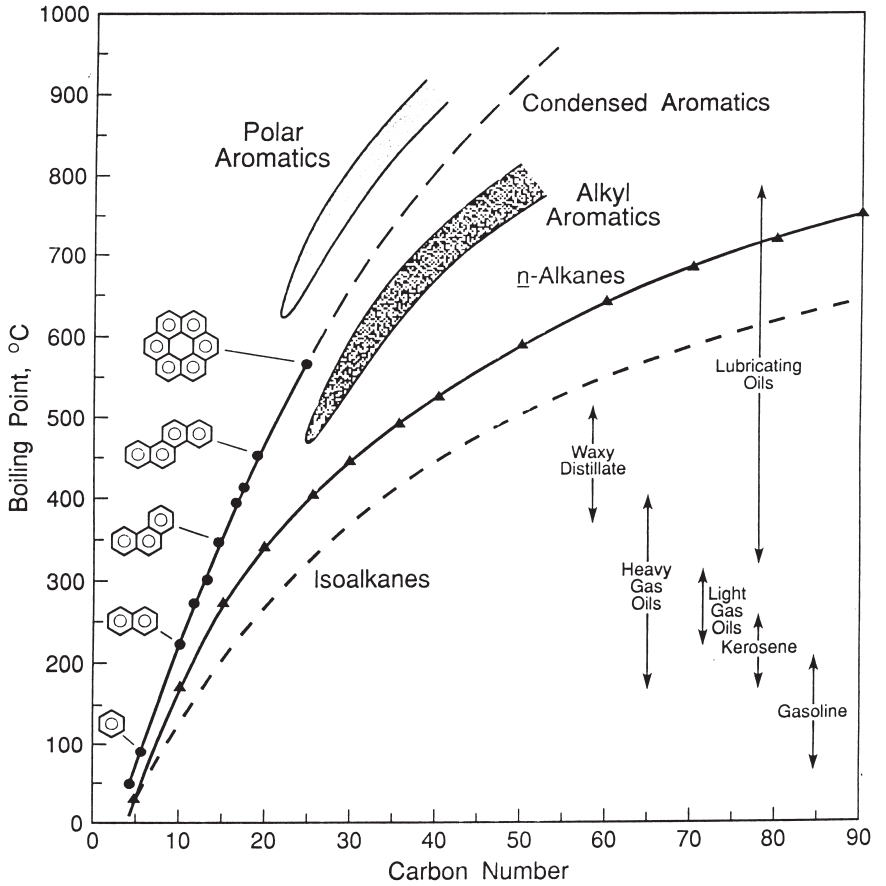

Figure 7.1. Boiling point and carbon number for various hydrocarbons and petroleum products

sulfur compounds. Generally, objectionable odors (mercaptans) are present (ASTM D-3227, IP 342), and these are removed by caustic washing or converted to odorless compounds by sweetening processes (Speight, 2000). After treatment, the kerosene streams are blended to meet specifications and the finished product is ready for marketing.

Chemically, kerosene is a mixture of hydrocarbons, and the constituents include *n*-dodecane (n-$C_{12}H_{26}$), alkyl benzenes, and naphthalene and its derivatives (ASTM D-1840). The chemical composition depends on its source and has a high number (>100,000) of isomers that are possible (Table 7.2). The actual number of compounds in kerosene is much lower, and there are claims to less than 100 constituents but that, again, is source- and process dependent.

Table 7.2. Increase in Number of Isomers with Carbon Number

Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

Kerosene, because of its use as burning oil, must be free of aromatic and unsaturated hydrocarbons as well as free of the more obnoxious sulfur compounds. The desirable constituents of kerosene are saturated hydrocarbons, and it is for this reason that kerosene is manufactured as a straight-run fraction, not by a cracking process.

7.3. TEST METHODS

Kerosene is composed chiefly of hydrocarbons containing 12 or more carbon atoms per molecule. Although the kerosene constituents are predominantly saturated materials, there is evidence for the presence of substituted tetrahydronaphthalenes. Dicycloparaffins also occur in substantial amounts in kerosene. Other hydrocarbons with both aromatic and cycloparaffin rings in the same molecule, such as substituted indane, also occur in kerosene. The predominant structure of the dinuclear aromatics appears to be that in which the aromatic rings are condensed, such as naphthalene, whereas the *isolated* two-ring compounds, such as biphenyl, are only present in traces, if at all (ASTM D-1840).

Low proportions of aromatic and unsaturated hydrocarbons are desirable to maintain the lowest possible level of smoke during burning. Although some aromatics may occur within the boiling range assigned to kerosene, excessive amounts can be removed by extraction; that kerosene

is not usually prepared from cracked products almost certainly excludes the presence of unsaturated hydrocarbons.

The essential properties of kerosene are flash point (ASTM D-56, ASTM D-93, ASTM D-3828, IP 34, IP 170, IP 303), distillation range (ASTM D86, ASTM D-1160, ASTM D-2887, ASTM D-6352), burning characteristics (ASTM D-187, IP 10), sulfur content (ASTM D-129, ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 61, IP 336, IP 373), color (ASTM D-156, ASTM D-1209, ASTM D-1500, ASTM D-1554, ASTM D-2392, ASTM D-3830, ASTM D-6045), and cloud point (ASTM D-2500, ASTM D-5772, ASTM D-5771, ASTM D-5773, IP 219). In the case of the flash point (ASTM D-56), the minimum flash temperature is generally placed above the prevailing ambient temperature; the fire point (ASTM D-92) determines the fire hazard associated with its handling and use.

7.3.1. Acidity

Acids can be present in kerosene aviation turbine fuels because of acid treatment during refining. These trace acid quantities are undesirable because of the possibility of metal corrosion and impairment of the burning characteristics and other properties of the kerosene. The potential for metals in kerosene is less than it is for aviations fuels, but several of the same tests can be applied (Chapter 6).

One test method (ASTM D-1093) is used solely for the qualitative determination of the acidity of hydrocarbon liquids and their distillation residues. The results are qualitative. Basicity determination can also be performed with a small change in the procedure (see below). In the test method, a sample is shaken with water and the aqueous layer is tested for acidity with methyl orange indicator (red color). Basicity can be determined with phenolphthalein indicator (pink color) instead of the methyl orange indicator.

Another test method (ASTM D-3242, IP 354) covers the determination of the acidity in an aviation turbine fuel in the range 0.000–0.100 mg potassium hydroxide/g, but the test is not suitable for determining significant acid contamination. In this test, a sample is dissolved in a solvent mixture (toluene plus isopropyl alcohol and a small amount of water) and under a stream of nitrogen is titrated with standard alcoholic *KOH* to the color change from orange in acid to green in base via added indicator *p*-naphtholbenzein solution.

7.3.2. Burning Characteristics

The ability of kerosene to burn steadily and cleanly over an extended period (ASTM D-187, IP 10) is an important property and gives some indi-

cation of the purity or composition of the product. The quality of a kerosene as a burning oil is related to its burning characteristics and is dependent on such factors as its composition, volatility, viscosity, calorific value, sulfur content, and freedom from corrosive substances or contaminants. This test method covers the qualitative determination of the burning properties of kerosene to be used for illuminating purposes. In the test, a kerosene sample is burned for 16 h in a specified lamp under specified conditions. The average rate of burning, the change in the shape of the flame, and the density and color of the chimney deposit are reported. A corresponding test method (IP 10) is used for the quantitative evaluation of the wick char-forming tendencies of kerosene.

However, the effect of hydrocarbon type composition is greater with wick-fed yellow flame burners than with wick-fed blue flame burners. With the former, kerosenes that are mainly paraffinic burn well in lamps with a poor draft, whereas under the same conditions kerosenes containing high proportions of aromatics and naphthenes burn with a reddish or even smoky flame.

The smoke point test (ASTM D-1319, ASTM D-1322, IP 57, IP 156) enables this property to be measured. In this test the oil is burned in a standard wick-fed lamp in which flame height can be varied against a background of a graduated scale. The maximum flame height in millimeters at which the oil burns without smoking under the standard conditions is termed the smoke point. Even if full advantage is not taken to utilize maximum nonsmoking flame height, the property of high smoke point ensures that in the event of sudden draft causing extension in flame height, there will be less tendency for smoking to occur in such circumstances. The smoke point test is also used in the assessment of the burning characteristics of certain aviation turbine fuels.

The 7-day burning test (IP 11) is used to evaluate the burning properties of oil for which long periods of uninterrupted and unattended burning may be necessary. The oil is burned for 7 days in a specified lamp under strictly controlled conditions. Every 24 h during the test the flame height is measured, and at the end of the test the condition of the wick and burner is also recorded. A corresponding test (ASTM D-219) is available in which a standard semaphore lamp is used. The test is continued until 650 ml of oil are burned, which usually takes about 5–6 days. At the end of the test, the change in the height of the flame and the condition of the wick and chimney are recorded.

The 24-h burning test (ASTM D-187) involves noting the average oil consumption, change in flame dimensions, and final appearance of wick and chimney. No quantitative determination of char value is made (IP-10). In this method the oil is burned for 24 h in the standard lamp with a flame initially adjusted to specified dimensions. The details of operation are carefully spec-

ified and involve the test room conditions, volume of sample, wick nature, pretreatment of wick and glass chimney, method of wick trimming, and procedure for removal of the char. At the conclusion of the test, the oil consumption and the amount of char formed on the wick are determined and the char value is calculated as milligrams per kilogram of oil consumed. A qualitative assessment of the appearance of the glass chimney is also made.

The considerable effect on char-forming tendency of even traces of high-boiling contaminants is demonstrated by the fact that the addition of 0.01% of a heavy lubricating oil to a kerosene of a char value of 103 mg/kg (the char value) can result in doubling that char value.

7.3.3. Calorific Value (Heat of Combustion)

The heat of combustion (ASTM D-240, ASTM D-1405, ASTM D-2382, ASTM D-2890, ASTM D-3338, ASTM D-4529, ASTM D-4809, ASTM D-6446, IP 12) is a direct measure of fuel energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter. A high calorific value is obviously desirable in oil used for heating purposes. Calorific value does not, however, vary greatly in the range of paraffinic-type kerosene (ASTM D-240, IP 12).

When an experimental determination of heat of combustion is not available and cannot be made conveniently, an estimate might be considered satisfactory (ASTM D-6446). In this test method the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the hydrogen content (ASTM D-1018, ASTM D-1217, ASTM D-1298, ASTM D-3701, ASTM D-4052, ASTM D-4808, ASTM D-5291 IP 160, IP 365), density (ASTM D-129, ASTM D-1250, ASTM D-1266, ASTM D-2622, ASTM D-3120, IP 61, IP 107), and sulfur content (ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 336, IP 373) of the sample are determined by experimental test methods and the net heat of combustion is calculated with the values obtained by these test methods based on reported correlations.

Another equation that can be used to calculate the heat of combustion is based on the specific gravity of the kerosene:

$$Q = 12{,}400 - 2{,}100d^2$$

where Q is the heat of combustion and d is the specific gravity. However, the accuracy of any method used to calculate such a property is not

guaranteed and can only be used as a guide to or approximation of the measured value.

An alternative criterion of energy content is the *aniline gravity product* (AGP), which is related to calorific value (ASTM D-1405, IP 193). The aniline gravity product is the product of the API gravity (ASTM D-287, ASTM D-1298) and the aniline point of the fuel (ASTM D-611, IP 2). The aniline point is the lowest temperature at which the fuel is miscible with an equal volume of aniline and is inversely proportional to the aromatic content. The relationship between the aniline gravity product and calorific value is given in the method. In another method (ASTM D-3338), the heat of combustion is calculated from the fuel density, the 10%, 50%, and 90% distillation temperatures, and the aromatic content. However, neither method is legally acceptable, and other methods (ASTM D-240, ASTM D-1655, ASTM D-4809) are preferred.

7.3.4. Composition

Because of the estimated (or real) number of isomers in this carbon number range (Table 7.2), complete speciation of individual hydrocarbons is not possible for middle distillates. Compositional analysis of middle distillates is obtained in terms of hydrocarbon group type totals. These groups are most often defined by a chromatographic separation.

Thus the first level of compositional information is group type totals as deduced by adsorption chromatography form the distribution of saturates, olefins, and aromatics in materials that boil below 315°C (600°F) (ASTM D-1319). Adsorption methods (ASTM D-2007) can also be used to determine hydrocarbon types in kerosene, but, with all adsorption methods, allowances must be made for the loss of volatile constituents during the workup procedure. Thus column chromatography would be best done with a stabilized (volatile constituents removed to a predetermined temperature) feedstock.

Burning oil kerosene contains three main types of hydrocarbons—paraffinic, naphthenic, and aromatic—with a preponderance of the paraffinic type. This is in contrast to *power kerosene*, or *tractor vaporizing oil*, which has a comparatively high content of aromatics and naphthenes favorable for high octane rating. It may also contain slight amounts of sulfur in the form of a variety of organic compounds.

Compositional analysis of kerosene distillates can also be obtained in terms of mass spectral Z-series (ASTM D-2425, ASTM D-2789, ASTM D-3239, ASTM D-6379). Mass spectrometry has been a powerful technique for hydrocarbon type analysis of middle distillates and can provide more compositional detail than chromatographic analysis. Hydrocarbon types are classified in terms of a Z-series. Z in the empirical formula C_nH2_{n+Z} is a

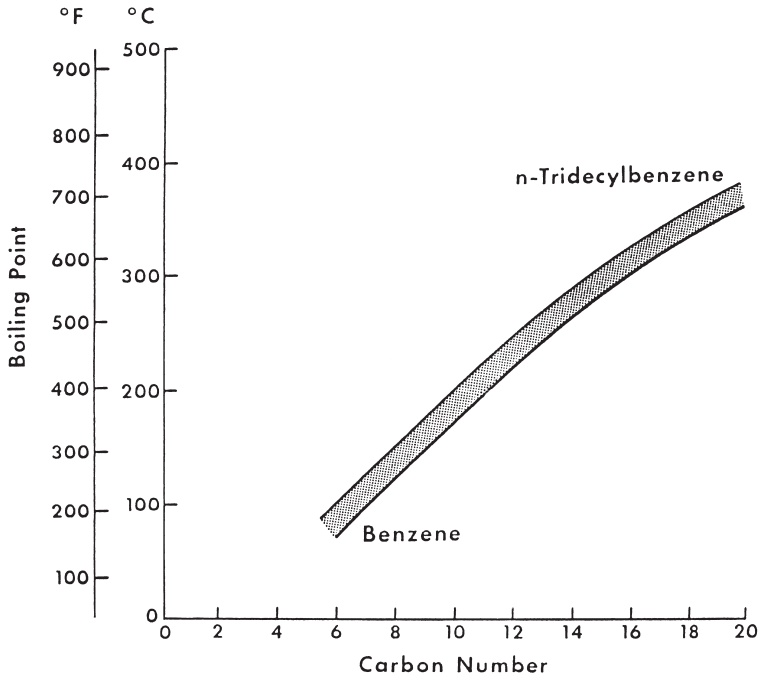

Figure 7.2. Effect of size of the alkyl chain on the boiling point of benzene

measure of the hydrogen deficiency of the compound (ASTM D-2425). This method requires that the sample be separated into saturate and aromatic fractions before mass spectrometric analysis. This separation is standardized (ASTM D-2549) and is applicable to kerosene.

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined by high-resolution nuclear magnetic resonance spectroscopy (ASTM D-5292), but the results from this test are not equivalent to mass- or volume-percent aromatics determined by the chromatographic methods. The chromatographic methods determine the percentage by weight (or the percentage by volume) of molecules that have one or more aromatic rings. Any alkyl substituents on the rings contribute to the percentage of aromatics determined by chromatographic techniques but the presence of an aromatic ring (no matter what the length of the alkyl side chain) dictates that the compound be isolated as an aromatic, thereby leading to erroneous estimates of the carbon atoms in aromatics systems.

Because the aromatic hydrocarbon content of aviation turbine fuels affects their combustion characteristics and smoke forming tendencies, the amounts of aromatics (ASTM D-1319, IP 156) are limited. Aromatic

constituents also increase the luminosity of the combustion flame (ASTM D-l740), which can adversely affect the life of the combustion chamber.

The aromatics content of kerosene can also be determined by a test method (ASTM D-5186) in which a small aliquot of the sample is injected onto a packed silica adsorption column and eluted with supercritical carbon dioxide as the mobile phase. Mono- and polynuclear aromatics in the sample are separated from nonaromatics and detected with a flame ionization detector. The chromatographic areas corresponding to the mono- and polynuclear and nonaromatic components are determined, and the mass percent content of each of these groups is calculated by area normalization. The results obtained by this method are at least statistically more precise than those obtained by other test methods (ASTM D-1319, ASTM D-2425).

In yet another test method for the determination of aniline point and mixed aniline point (ASTM D-611, IP 2), the proportions of the various hydrocarbon constituents of kerosene can be determined. This test is most often used to estimate the aromatic content of kerosene. Aromatic compounds exhibit the lowest aniline points and paraffin compounds have the highest aniline points, with cycloparaffins (naphthenes) and olefins having aniline points between the two extremes. In any homologous series the aniline point increases with increasing molecular weight.

There are five submethods in the test (ASTM D-611, IP 2) for the determination of the aniline point: (1) Method A is used for transparent samples with an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture; (2) method B, a thin film method, is suitable for samples too dark for testing by method A; (3) methods C and D are used when there is the potential for sample vaporization at the aniline point; (4) method D is particularly suitable where only small quantities of sample are available; and (5) method E uses an automatic apparatus suitable for the range covered by methods A and B.

Olefins in kerosene also influence the burning characteristics and can be determined by the bromine number (ASTM D-1159, ASTM D-2710, IP 130). The bromine number is the number of grams of bromine that will react with 100 g of the sample under the test conditions. The magnitude of the bromine number is an indication of the quantity of bromine-reactive constituents and is not an identification of constituents. It is used as a measure of aliphatic unsaturation in petroleum samples and as percentage of olefins in petroleum distillates boiling up to approximately 315°C (600°F). In this test, a known weight of the sample dissolved in a specified solvent maintained at 0–5°C (32–41°F) is titrated with standard bromide-bromate solution. Determination of the end point is method dependent.

Gas chromatography (ASTM D-2427, ASTM D-4420, ASTM D-5443, ASTM D-5580) remains the most reliable method for the determination of

hydrocarbon types, including olefins (ASTM D-6296), in kerosene and similar-boiling fractions. In particular, methods in which a combination of gas chromatography and Fourier transform infrared spectroscopy (GC-FTIR) (ASTM D-5986) and gas chromatography and mass spectrometry (GC-MS) (ASTM D-5769) are finding increased use. Indeed, Fourier transform infrared spectroscopy has been used to predict properties such as density, freezing point, flash point, aromatics content, initial boiling point, final boiling point, and viscosity (Garrigues et al., 1995). The data have a high degree of repeatability and reproducibility.

The significance of the total sulfur content of kerosene varies greatly with the type of oil and the use to which it is put. Sulfur content is of great importance when the oil to be burned produces sulfur oxides that contaminate the surroundings. Only slight amounts of sulfur compounds remain in kerosene after refining. Refining treatment includes among its objects the removal of such undesirable products as hydrogen sulfide, mercaptan sulfur, and *free* or corrosive sulfur. Hydrogen sulfide and mercaptans cause objectionable odors, and both are corrosive. Their presence can be detected by the Doctor test (ASTM D-484, ASTM D-4952, IP 30). The Doctor test (which is pertinent for petroleum product specifications; ASTM D-235) ensures that the concentration of these compounds is insufficient to cause such problems in normal use. In this test, the sample is shaken with sodium plumbite solution, a small quantity of sulfur is added, and the mixture is shaken again. The presence of mercaptans, hydrogen sulfide, or both is indicated by discoloration of the sulfur floating at the oil-water interface or by discoloration of either of the phases.

Free, or corrosive, sulfur in an appreciable amount could result in corrosive action on the metallic components of an appliance. Corrosive action is of particular significance in the case of pressure burner vaporizing tubes that operate at high temperatures. The usual test applied in this connection is the corrosion (copper strip) test (ASTM D-130, ASTM D-849, IP 154).

The copper strip test methods are used to determine the corrosiveness to copper of gasoline, diesel fuel, lubricating oil, or other hydrocarbons. Most sulfur compounds in petroleum are removed during refining. However, some residual sulfur compounds can have a corroding action on various metals. This effect is dependent on the types of sulfur compounds present. The copper strip corrosion test measures the relative degree of corrosivity of a petroleum product.

One method (ASTM D-130, IP 154) uses a polished copper strip immersed in a given quantity of sample and heated at a temperature and for a time period characteristic of the material being tested. At the end of this period the copper strip is removed, washed, and compared with the copper strip corrosion standards (ASTM, 2001). This is a pass/fail test. In another method (ASTM D-849), a polished copper strip is immersed in

200 ml of specimen in a flask with a condenser and placed in boiling water for 30 min. At the end of this period, the copper strip is removed and compared with the ASTM copper strip corrosion standards. This is also a pass/fail test.

It is important that the total sulfur content of burning oil should be low (ASTM D-1266, IP 107). All the sulfur compounds present in an oil are converted to oxides of sulfur during burning. These oxides of sulfur should not be present to a harmful extent in the immediate atmosphere, and this applies particularly to indoor burning appliances that are not provided with a flue. Also, it has been indicated above that a high total sulfur content of an oil can contribute to the formation of lamp chimney deposits.

Gas chromatography with either sulfur chemiluminescence detection or atomic emission detection has been used for sulfur-selective detection. Selective sulfur and nitrogen gas chromatographic detectors, exemplified by the flame photometric detector (FPD) and the nitrogen-phosphorus detector (NPD), have been available for many years. However, these detectors have limited selectivity for the element over carbon, exhibit nonuniform response, and have other problems that limit their usefulness.

Nitrogen compounds in middle distillates can be selectively detected by chemiluminescence. Individual nitrogen compounds can be detected down to 100 ppb nitrogen.

Correlative methods have long been used as a way of dealing with the complexity of petroleum fractions. Relatively easy to measure physical properties such as density, viscosity, and refractive index (ASTM D-1218) have been correlated to hydrocarbon structure (Table 7.3) with the potential to relate refractive index data to the nature of the constituents of a petroleum product.

In recent years an entirely new class of correlative methods has been developed. These use near-infrared (NIR) or mid-infrared spectra together

Table 7.3. Refractive Indexes of Selected Hydrocarbons

Compound	Refractive Index n_D^{20}
n-Pentane	1.3578
n-Hexane	1.3750
n-Hexadecane	1.4340
Cyclopentane	1.4065
Cyclopentene	1.4224
Pentene-1	1.3714
1,3-Pentadiene	1.4309
Benzene	1.5011
cis-Decahydronaphthalene	1.4814
Methylnaphthalenes	1.6150

with sophisticated chemometric techniques to predict a wide variety of properties. Properties such as composition (saturates, aromatics), freezing point, density, viscosity, aromatics, and heat of combustion have been successfully predicted.

It is important to recognize that these methods are correlations and should not be used to estimate properties that are outside the calibration set.

The *color* of kerosene is of little significance, but a product darker than usual may have resulted from a change in composition because of contamination or aging and in fact a color darker than specified (ASTM D-l56) may be considered by some users as unsatisfactory. Finally, the cloud point of kerosene (ASTM D-2500) gives an indication of the temperature at which the wick may become coated with wax particles, thus lowering the burning qualities of the oil.

Alternatively, the wax appearance point (ASTM D-3117) may also be determined as a means of estimating the composition of kerosene in terms of the wax (*n*-paraffins) content. The wax appearance point is the temperature at which wax crystals begin to precipitate from a fuel. In this test (ASTM D-3117), a sample is cooled under prescribed conditions with stirring. The temperature at which wax first appears is the wax appearance point.

7.3.5. Density (Specific Gravity)

Density (specific gravity) is an important property of petroleum products and is often part of product specifications (Table 7.4). Materials are usually bought and sold on this basis or, if on a volume basis, then converted to a mass basis via density measurements. This property is almost synonymously termed as density (mass of liquid per unit volume), specific gravity (the ratio of the mass of a given volume of liquid to the mass of an equal volume of pure water at the same temperature), and relative density (same as specific

Table 7.4. Specific Gravity and API Gravity of Crude Oil and Selected Products

Material	Specific Gravity 60°/60°F	API Gravity, deg
Crude oils	0.65–1.06	87–2
Casinghead liquid	0.62–0.70	97–70
Gasoline	0.70–0.77	70–52
Kerosene	0.77–0.82	52–40
Lubricating oil	0.88–0.98	29–13
Residua and cracked residua	0.88–1.06	29–2

gravity). Usually a hydrometer, pycnometer, or digital density meter is used in these standards (ASTM, 2000).

Specific gravity has no relation to burning quality but is a useful aid in checking consistency of production of a particular grade. The specific gravity of kerosene can be determined very conveniently by the hydrometer method (ASTM D-1298, IP 160).

7.3.6. Flash Point

The flash point is a guide to the fire hazard associated with the use of kerosene; it can be determined by several test methods, and the results are not always strictly comparable. Generally, the flash point of kerosene is specified as being in excess of 38°C (100°F) because of production as well as safety considerations.

The minimum flash point is usually defined by the Abel method (IP 170), except for high-flash kerosene, where the Pensky-Martens method (ASTM D-93, IP 34) is specified. The TAG method (ASTM D-56) is used for both the minimum and maximum limits, whereas certain military specifications also give minimum limits by the Pensky-Martens method (ASTM D-93, IP 34). The Abel method (IP 170) can give results up to 2–3°C (3–5°F) lower than the TAG method (ASTM D-56).

7.3.7. Freezing Point

The freezing point of kerosene is not of the same importance as the freezing point of aviation fuel (Chapter 6) but deserves mention because of its influence on kerosene use.

Three test methods are available for determination of the freezing point. All three methods have been found to give equivalent results. However, when a specification calls for a specific test, only that test must be used.

In the first test (ASTM D-2386, IP 16), a measured fuel sample is placed in a jacketed sample tube also holding a thermometer and a stirrer. The tube is placed in a vacuum flask containing the cooling medium. Various coolants used are acetone, methyl alcohol, ethyl alcohol, or isopropyl alcohol, solid carbon dioxide, or liquid nitrogen. As the sample cools, it is continuously stirred. The temperature at which the hydrocarbon crystals appear is recorded. The jacketed sample is removed from the coolant and allowed to warm, under continuous stirring. The temperature at which the crystals completely disappear is recorded.

In the second test (ASTM D-5901, IP 434), an automated optical method is used for the temperature range to –70°C (–94°F). In this method, a 25-min portion of the fuel is placed in a test chamber that is cooled while continuously being stirred and monitored by an optical system. The

temperature of the specimen is measured with an electronic measuring device, and the temperatures when crystals first appear and then, on warming, disappear are recorded.

In the third method (ASTM D-5972, IP 435), an automated phase transition method is used in the temperature range –80 to 20°C (–112°F to 68°F). In this test, a specimen is cooled at a rate of 15 ± 5°C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an array of optical detectors for the first formation of solid hydrocarbon crystals. After that the specimen is warmed at the rate of 10 ± 0.5°C/min until all crystals return to the liquid phase, and that temperature is also recorded.

7.3.8. Pour Point

The *pour point* should not be confused with the *freezing point*. The *pour point* 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. Pour point data can be used to supplement other measurements of cold flow behavior, and the data are particularly useful for 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 characteristics. 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 operations. 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.

7.3.9. Smoke Point

Although a low smoke point is undesirable in that it may not give a satisfactory range of smokeless performance, a high smoke point alone is no guarantee that a kerosene has generally satisfactory burning characteristics. The smoke point test adequately reflects the essential feature of hydrocarbon type composition in relation to burning characteristics, as already indicated, and consequently no analysis for composition is necessary in the normal evaluation of burning oils.

Kerosene can vary widely in its burning quality as measured by carbon deposition, smoke formation, and flame radiation. This is a function of hydrocarbon composition—paraffins have excellent burning properties, in contrast to those of the aromatics (particularly the polynuclear aromatic hydrocarbons). As a control measure the smoke point test (ASTM D-l322, IP 57) gives the maximum smokeless flame height in millimeters at which the fuel will burn in a wick-fed lamp under prescribed conditions. The combustion performance of wide-cut fuels correlates well with smoke point when a fuel volatility factor is included, because carbon formation tends to increase with boiling point. A minimum smoke volatility index (SVI) value is specified and is defined as:

$$\text{SVI} = \text{smoke point} + 0.42\ (\text{percent distilled below } 204^\circ\text{C}/400^\circ\text{F}).$$

However, the smoke point is not always a reliable criterion of combustion performance and should be used in conjunction with other properties. Various alternative laboratory test methods have previously been specified such as the lamp burning test (ASTM D-187, IP 10) and a limit on the polynuclear aromatic content (ASTM D-1840), as well as the luminometer number (ASTM D-l740). The test apparatus is a smoke point lamp modified to include a photoelectric cell for flame radiation measurement and a thermocouple to measure temperature rise across the flame. The fuel luminometer number (LN) is expressed on an arbitrary scale on which values of 0 to 100 are given to the reference fuels tetralin and *iso*-octane, respectively.

7.3.10. Viscosity

The kinematic viscosity of many petroleum fuels is important for their proper use, for example, flow of fuels through pipelines, injection nozzles, and orifices, and the determination of the temperature range for proper operation of the fuel in burners.

The quantity of oil flowing up a wick is related to the height of the top of the wick above the level of oil in the container and the viscosity and surface

tension of the oil. Viscosity (ASTM D-445, IP 71) is more significant in this respect than surface tension, because it varies more in magnitude than the latter with different kerosenes and with change of temperature.

7.3.11. Volatility

An abnormally high final boiling point and percentage residue of a kerosene may indicate contamination with higher-boiling constituents, although the presence of trace quantities of very heavy oils sufficient to cause high char values might not necessarily be revealed by these features. Thus the boiling range of kerosene is an important aspect of kerosene properties.

The boiling range (ASTM D-86, IP 123) is of less importance for kerosene than for gasoline, but it is an indication of the viscosity of the product, for which there is no requirement for kerosene. The nature of the distillation range (ASTM D-86, IP 123) is of significance with regard to burning characteristics. It can control the flash point and viscosity, the effect of which has already been mentioned. The initial boiling point and the 10% point chiefly affect the flash point and ease of ignition, whereas the mid-boiling point is more relevant to the viscosity.

Another test method (ASTM D-6352) that can be used for product specification testing is applicable to petroleum distillate fractions with an initial boiling point of <700°C (<1292°F) at atmospheric pressure. This test method extends the scope of other test methods (ASTM D-D 86, ASTM D-1160, ASTM D-2887) to boiling range determination by gas chromatography. In the method, a nonpolar open tubular capillary gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. A sample aliquot diluted with a viscosity-reducing solvent is introduced into the chromatographic system. The column oven temperature is raised at a specified linear rate to effect separation of the hydrocarbon components. The detector signal is recorded as area slices for consecutive retention time intervals during the analysis. Retention times of known normal paraffin hydrocarbons spanning the scope of the test method are used for normalizing the retention times of the unknown mixture area slices.

Contamination of kerosene with heavy oil may also be revealed by the test method that is used to determine the amount of residue left by evaporation (ASTM D-381, IP 131), although this depends on the relative volatility of the contaminant.

One of the most important physical parameters defining these products is their boiling range distribution, which can be determined using a low-efficiency, one-theoretical plate distillation procedure (ASTM D-86). This has been adequate for product specification purposes; however, engineer-

ing studies require true boiling point (TBP) data (ASTM D-2887, ASTM D-2892).

The vapor pressure of petroleum products at various vapor-to-liquid ratios is an important physical property for shipping and storage. Although determining the volatility of kerosene is usually accomplished through a boiling range distribution (ASTM D-86, IP 123), determination of the Reid vapor pressure (ASTM D-323, IP 69) can also be used along with several other methods (ASTM D-5190, ASTM D-5482, ASTM D-6378).

7.3.12. Water and Sediment

Kerosene, because of its higher density and viscosity, tends to retain fine particulate matter and water droplets in suspension for a much longer time than gasoline. Free water in kerosene can be detected by the use of a Dean and Stark adaptor (ASTM D-4006, IP 358) (Fig. 7.3), by the Karl Fischer titration method (ASTM D-1744, ASTM D-6304), by the distillation method (ASTM D-95, IP 74), or by a series of alternate tests (ASTM D-4176, ASTM D-4860). The standard water reaction test method (ASTM D-1094, IP 289) can also be used.

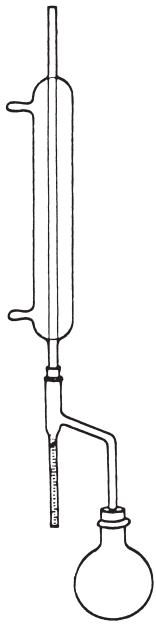

Figure 7.3. A Dean and Stark adaptor on the bottom of a condenser

In addition to water, sediment can also occur and will cause fouling of the fuel handling facilities and the fuel system. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of kerosene during use, and a test method is available to determine the water and sediment in fuels (ASTM D-2709). In the test method, a sample of kerosene is centrifuged at a rcf of 800 for 10 min at 21–32°C in a centrifuge tube readable to 0.005 ml and measurable to 0.01 ml. After centrifugation, the volume of water and sediment that has settled into the tip of the centrifuge tube is read to the nearest 0.005 ml.

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CHAPTER

8

DIESEL FUEL

8.1. INTRODUCTION

Kerosene, diesel fuel, and aviation turbine fuel (jet fuel) are members of the class of petroleum products known as middle distillates (Gruse and Stevens, 1960; Guthrie, 1967; Kite and Pegg, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Hemighaus, 1998; Speight, 1999; Heinrich and Duée, 2000). As the name implies, these products are higher boiling than gasoline but lower boiling than gas oil. Middle distillates cover the boiling range from approximately 175 to 375°C (350–700°F) and the carbon number range from about C_8 to C_{24}. These products have similar properties but different specifications as appropriate for their intended use.

The broad definition of fuels for land and marine diesel engines and for nonaviation gas turbines covers many possible combinations of volatility, ignition quality, viscosity, gravity, stability, and other properties. Various specifications are used to characterize these fuels (ASTM D-975, ASTM D-2880).

8.2. PRODUCTION AND PROPERTIES

Diesel fuels originally were straight-run products obtained from the distillation of crude oil. Currently, diesel fuel may also contain varying amounts of selected cracked distillates to increase the volume available. The boiling range of diesel fuel is approximately 125–328°C (302–575°F) (Table 8.1). Thus, in terms of carbon number and boiling range, diesel fuel occurs predominantly in the kerosene range (Chapter 7), and thus many of the test methods applied to kerosene can also be applied to diesel fuel. Diesel fuel depends on the nature of the original crude oil, the refining processes by which the fuel is produced, and the additive (if any) used, such as the solvent red dye (ASTM D-6258). Furthermore, the specification for diesel fuel can exist in various combinations of characteristics such as, for example, volatility, ignition quality, viscosity, gravity, and stability.

One of the most widely used specifications (ASTM D-975) covers three grades of diesel fuel oils, No. l-D, No. 2-D, and No. 4-D. Grades No. l-D and

Table 8.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

2-D are distillate fuels (ASTM D-975), the types most commonly used in high-speed engines of the mobile type, in medium speed stationary engines, and in railroad engines. Grade 4-D covers the class of more viscous distillates and, at times, blends of these distillates with residual fuel oils. The marine fuel specifications (ASTM D-2069) have four categories of distillate fuels and fifteen categories of fuels containing residual components.

Additives may be used to improve the fuel performance, and additives such as alkyl nitrates and nitrites (ASTM D-1839, ASTM D-4046) can improve ignition quality. Pour point depressants can improve low-temperature performance. Antismoke additives reduce exhaust smoke, which is of growing concern as more and more attention is paid to atmospheric pollution. Antioxidant and sludge dispersants may also be used, particularly with fuels formulated with cracked components, to prevent the formation of insoluble compounds that could cause line and filter plugging (ASTM D-2068, ASTM D-6371, IP 309).

8.3. TEST METHODS

As for all fuels, the properties of a product define the ability to serve a stated purpose. Once the required properties are determined, they are controlled by appropriate tests and analyses. The quality criteria and methods for testing fuels for land and marine diesel engines, such as the cetane number, apply to both fuels.

8.3.1. Acidity

Petroleum products may contain acidic constituents that are present as additives or as degradation products, such as oxidation products. The relative amount of these constituents can be determined by titrating a sample of the product with base, and the *acid number* is a measure of the amount of acidic substances in the product under the conditions of the test.

One of the test methods (ASTM D-664) resolves constituents into groups having weak-acid and strong-acid ionization properties. In this test method, 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 by 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. The test method may be used to indicate relative changes that occur in diesel fuel under oxidizing conditions regardless of the color or other properties of the resulting oil. There are three other test methods for the determination of acid numbers (ASTM D-974, ASTM D-3339, ASTM D-4739) that are used to measure the inorganic and total acidity of the fuel and indicate its tendency to corrode metals that it may contact.

8.3.2. Appearance and Odor

The general *appearance*, or *color*, of diesel fuel is a useful indicator against contamination by residual (higher boiling) constituents, water, or fine solid particles. Therefore, it is necessary to make a visual inspection that clear fuel is being delivered (ASTM D-4176).

Color, being part of the appearance of diesel fuel, should also be determined because the color of petroleum products is used for manufacturing control purposes. In some cases the color may serve as an indication of the degree of refinement of the material. Several color scales are used for determination (ASTM D-156, ASTM D-1209, ASTM D-1500, ASTM D-1544, IP 196). Typically the methods require a visual determination of color with colored glass disks or reference materials.

Similarly, acceptance is important with regard to *odor*, and it is usually required that diesel fuel is reasonably free of contaminants, such as mercaptans, which impart unpleasant odors to the fuel (ASTM D-4952, IP 30).

8.3.3. Ash

Small amounts of unburnable material are found in diesel fuel in the form of soluble metallic soaps and solids, and these materials are designated as

ash, although "ash-forming constituents" is a more correct term. In the test for the quantitative determination of ash-forming constituents (ASTM D-482, IP 4), a small sample of fuel is burned in a weighed container until all of the combustible matter has been consumed as indicated by the residue and container attaining a constant weight. The amount of unburnable residue is the ash content and is reported as percent by weight of the sample.

The ash-forming constituents in diesel fuel (ASTM D-2880) are typically so low that they do not adversely affect gas turbine performance, unless such corrosive species as sodium, potassium, lead, or vanadium are present. However, there are recommendations for the storage and handling of these fuels (ASTM D-4418) to minimize potential contamination.

Vanadium can form low-melting compounds such as vanadium pentoxide, which melts at 691°C (1275°F) and causes severe corrosive attack on all of the high-temperature alloys used for gas-turbine blades and diesel engine valves. If there is sufficient magnesium in the fuel, it will combine with the vanadium to form compounds with higher melting points and thus reduce the corrosion rate to an acceptable level. The resulting ash will form deposits in the turbine, but the deposits are self-spalling when the turbine is shut down. The use of a silicon-base additive will further reduce the corrosion rate by absorption and dilution of the vanadium compounds.

Sodium and potassium can combine with vanadium to form eutectics, which melt at temperatures as low as 565°C (1050°F), and with sulfur in the fuel to yield sulfates with melting points in the operating range of the gas turbine. These compounds produce severe corrosion for turbines operating at gas inlet temperatures above 649°C (1200°F). Thus the amount of sodium plus potassium must be limited. For gas turbines operating below 649°C (1200°F), the corrosion due to sodium compounds is of lesser importance and can be further reduced by silicon-base additive.

Calcium is not as harmful and may even serve to inhibit the corrosive action of vanadium. However, the presence of calcium can lead to deposits that are not self-spalling when the gas turbine is shut down and not readily removed by water washing of the turbine. Lead can cause corrosion, and, in addition, it can spoil the beneficial inhibiting effect of magnesium additives on vanadium corrosion. Because lead is only found rarely in significant quantities in crude oils, its presence in the fuel oil is primarily the result of contamination during processing or transportation.

8.3.4. Calorific Value (Heat of Combustion)

The heat of combustion (ASTM D-240, ASTM D-1405, ASTM D-2382, ASTM D-2890, ASTM D-3338, ASTM D-4529, ASTM D-4809, ASTM D-4868, ASTM D-6446, IP 12) is a direct measure of fuel energy content and

is determined as the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter. There are two heats of combustion, or calorific values, for every petroleum fuel, gross and net. When hydrocarbons are burned one of the products of combustion is water vapor, and the difference between the two calorific values is that the gross value includes the heat given off by the water vapor in condensing whereas the net value does not include this heat.

When an experimental determination of heat of combustion is not available and cannot be made conveniently, an estimate might be considered satisfactory (ASTM D-6446). In this test method the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the hydrogen content (ASTM D-1018, ASTM D-1217, ASTM D-1298, ASTM D-3701, ASTM D-4052, ASTM D-4808, ASTM D-5291 IP 160, IP 365), density (ASTM D-129, ASTM D-1250, ASTM D-1266, ASTM D-2622, ASTM D-3120, IP 61, IP 107), and sulfur content (ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 336, IP 373) of the sample are determined by experimental test methods, and the net heat of combustion is calculated with the values obtained by these test methods based on reported correlations.

An alternative criterion of energy content is the *aniline gravity product* (AGP), which is related to calorific value (ASTM D-1405, IP 193). The aniline gravity product is the product of the API gravity (ASTM D-287, ASTM D-1298) and the aniline point of the fuel (ASTM D-611, IP 2). The aniline point is the lowest temperature at which the fuel is miscible with an equal volume of aniline and is inversely proportional to the aromatic content. The relationship between the aniline gravity product and calorific value is given in the method. In another method (ASTM D-3338), the heat of combustion is calculated from the fuel density, the 10%, 50%, and 90% distillation temperatures, and the aromatic content. However, neither method is legally acceptable, and other methods (ASTM D-240, ASTM D-1655, ASTM D-4809) are preferred.

8.3.5. Carbon Residue

The carbon residue of a petroleum product serves as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat. In the current context, carbon residue test results are widely quoted in diesel fuel specifications. However, distillate diesel fuels that are satisfactory in other respects do not have high Conradson carbon residue values, and the test is chiefly used on residual fuels.

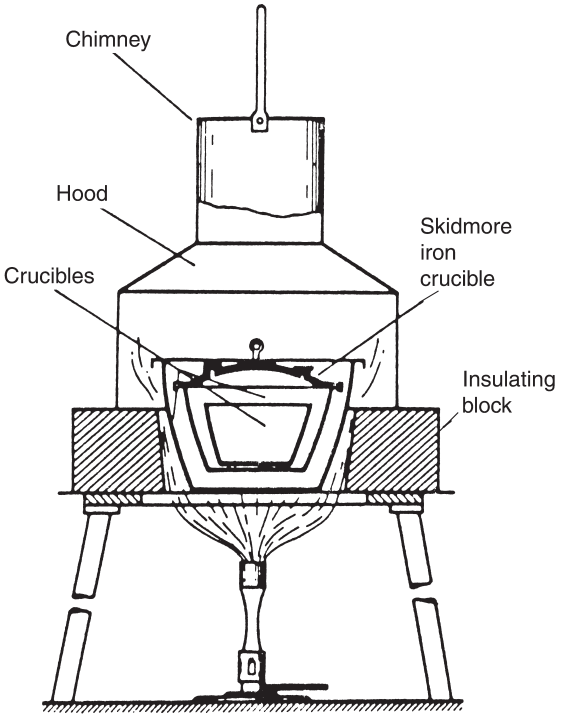

Figure 8.1. Apparatus for the determination of the Conradson carbon residue (ASTM D-189, IP 13)

Tests for Conradson carbon residue (ASTM D-189, IP 13) (Fig. 8.1), the Ramsbottom carbon residue (ASTM D-524, IP 14), and the microcarbon carbon residue (ASTM D-4530, IP 398) are often included in specification data for diesel fuel. 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.

8.3.6. Cetane Number and Cetane Index

The cetane number is an important property of diesel fuel. In the majority of diesel engines, the ignition delay period is shorter than the duration of injection. Under such circumstances, the total combustion period can be considered to be divided into the following four stages: (1) ignition delay, (2) rapid pressure rise, (3) constant pressure or controlled pressure rise, and (4) burning on the expansion stroke.

The cetane number of a diesel fuel is the numerical result of an engine test designed to evaluate fuel ignition delay. To establish the cetane number

scale, two reference fuels were selected. One, normal cetane, has excellent ignition qualities and, consequently, a very short ignition delay. A cetane number of 100 was arbitrarily assigned to this fuel. The second fuel, α-methylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. α-Methylnaphthalene has been replaced as a primary reference fuel by heptamethylnonane, which has a cetane number of 15 as determined by use of the two original primary reference fuels.

To determine the cetane number of any fuel, its ignition delay is compared in a standard test engine with a blend of reference fuels (ASTM D-613, IP 41).

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (cetane No. 100) in a blend with heptamethylnonane (cetane No. = 15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number:

$$\text{cetane number} = \%\ n\text{-cetane} + 0.15\ (\%\ \text{heptamethylnonane})$$

The shorter the ignition delay period, the higher the cetane number of the fuel and the smaller the amount of fuel in the combustion chamber when the fuel ignites. Consequently, high-cetane-number fuels generally cause lower rates of pressure rise and lower peak pressures, both of which tend to lessen combustion noise and to permit improved control of combustion, resulting in increased engine efficiency and power output.

In addition to the above, higher-cetane-number fuels tend to result in easier starting, particularly in cold weather, and faster warm-up. The higher-cetane-number fuels also usually form softer and hence more readily purged combustion chamber deposits and result in reduced exhaust smoke and odor. High-speed diesel engines normally are supplied with fuels in the range of 45–55 cetane number.

Because the determination of cetane number by engine testing requires special equipment, as well as being time-consuming and costly, alternative methods have been developed for calculating estimates of cetane number. The calculations are based on equations involving values of other known characteristics of the fuel.

One of the most widely used methods is based on the calculated cetane index formula. This formula represents a method for estimating the cetane number of distillate fuels from API gravity and mid-boiling point. The index value as computed from the formula is designated as a calculated cetane index (ASTM D-976, IP 218). Because the formula is complicated in its manipulation, a nomograph based on the equation has been developed for its solution.

8.3.7. Cloud Point

Under low-temperature conditions, paraffinic constituents of diesel fuel may be precipitated as a wax. This settles out and blocks the fuel system lines and filters, causing malfunctioning or stalling of the engine. The temperature at which the precipitation occurs depends on the origin, type, and boiling range of the fuel. The more paraffinic the fuel, the higher the precipitation temperature and the less suitable the fuel for low-temperature operation.

The temperature at which wax is first precipitated from solution can be measured by the cloud point test (ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP 219). The cloud point of a diesel fuel is a guide to the temperature at which it may clog filter systems and restrict flow. Cloud point is becoming increasingly important for fuels used in high-speed diesel engines, especially because of the tendency to equip such engines with finer filters. The finer the filter, the more readily it will become clogged by small quantities of precipitated wax. Larger fuel lines and filters of greater capacity reduce the effect of deposits from the fuel and therefore widen the cloud point range of fuels that can be used.

In the simple cloud point test method (ASTM D-2500), the sample is first heated to a temperature above the expected cloud point and then cooled at a specified rate and examined periodically. The temperature at which haziness is first observed at the bottom of the test jar is recorded as the cloud point.

8.3.8. Composition

The chemical composition of diesel fuel is extremely complex, with an enormous number of compounds normally present (Table 8.2). For this reason, it usually is not practical to analyze diesel fuel for individual compounds but it is often advantageous to define the compounds present as broad classifications of compound types, such as aromatics, paraffins, naphthenes and olefins.

One of the most important physical parameters defining diesel fuel, and other middle distillate products, is the boiling range distribution (ASTM D-86, ASTM D-2887, ASTM D-2892). However, the first major level of compositional information is group-type totals as deduced by adsorption chromatography (ASTM D-1319) (Fig. 8.2) to give volume percent saturates, olefins, and aromatics in materials that boil below 315°C (600°F). Following from this separation, the compositional analysis of diesel fuel and other middle distillates is then determined by a mass spectral Z series on which Z in the empirical formula C_nH_{2n+Z} is a measure of the hydrogen deficiency of the compound (ASTM D-2425, ASTM D-2786, ASTM D-3239,

Table 8.2. Increase in Number of Isomers with Carbon Number

Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

ASTM D-6379). Mass spectrometry can provide more compositional detail than chromatographic analysis. However, this method requires that the sample be separated into saturate and aromatic fractions (ASTM D-2549) before mass spectrometric analysis. This separation is applicable to diesel fuel but not to jet fuel, because it is impossible to evaporate the solvent used in the separation without also losing the light ends of the jet fuel.

The aromatic hydrocarbon content of diesel fuel affects the cetane number and exhaust emissions. One test method (ASTM D-5186) is applicable to diesel fuel and is unaffected by fuel coloration. Aromatics concentration in the range 1–75 mass% and polynuclear aromatic hydrocarbons in the range 0.5–50 mass% can be determined by this test method. In the method, a small aliquot of the fuel sample is injected onto a packed silica adsorption column and eluted with supercritical carbon dioxide mobile phase. Mono- and polynuclear aromatics in the sample are separated from nonaromatics and detected with a flame ionization detector. The detector response to hydrocarbons is recorded throughout the analysis time. The chromatographic areas corresponding to the mononuclear aromatic constituents, polynuclear aromatic constituents, and nonaromatic constituents are determined ,and the mass-percent content of each of these groups is calculated by area normalization.

Whereas nuclear magnetic resonance can be used to determine mass-percent hydrogen in diesel fuel (ASTM D-3701, ASTM D-4808), the percentage of aromatic hydrogen atoms and aromatic carbon atoms can be

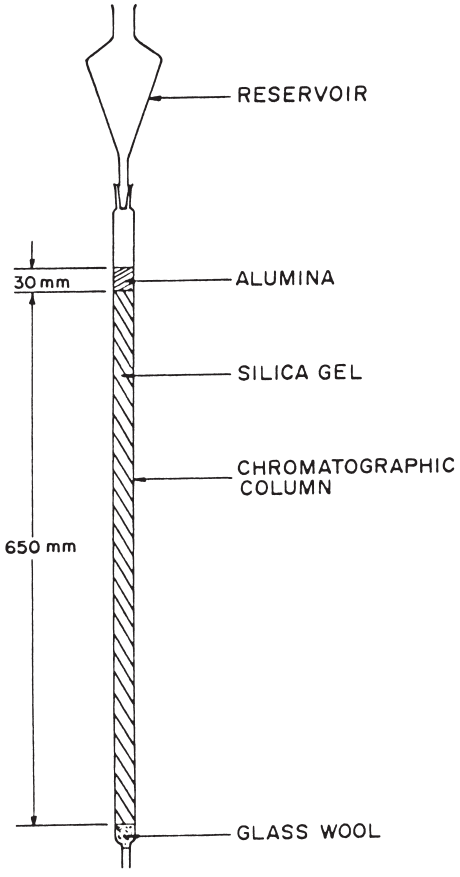

Figure 8.2. Apparatus for adsorption chromatography

determined by high-resolution nuclear magnetic resonance (ASTM D-5292). However, the results from this test are not equivalent to mass- or volume-percent aromatics determined by the chromatographic methods. The chromatographic methods determine the mass or volume percentage of molecules that have one or more aromatic rings. Any alkyl substituents on the rings contribute to the percentage of aromatics determined by chromatographic techniques.

The significance of the total sulfur content of diesel fuel cannot be overestimated and is of great importance because of the production of sulfur oxides that contaminate the surroundings. Generally, only slight amounts of sulfur compounds remain in diesel fuel after refining, and the diesel fuel must meet sulfur specification. However, with the planned reduc-

tion of sulfur in future specifications, sulfur detection becomes even more important.

Refining treatment includes among its objects the removal of such undesirable products as hydrogen sulfide, mercaptan sulfur, and *free* or corrosive sulfur. Hydrogen sulfide and mercaptans cause objectionable odors, and both are corrosive. The presence of such compounds can be determined by the Doctor test (ASTM D-484, ASTM D-4952, IP 30). The Doctor test (which is pertinent for petroleum product specifications; ASTM D-235) ensures that the concentration of these compounds is insufficient to cause such problems in normal use. In the test, the sample is shaken with sodium plumbite solution, a small quantity of sulfur is added, and the mixture is shaken again. The presence of mercaptans, hydrogen sulfide, or both is indicated by discoloration of the sulfur floating at the oil-water interface or by discoloration of either of the phases.

Free, or corrosive, sulfur in appreciable amount could result in corrosive action on the metallic components of an appliance. Corrosive action is of particular significance in the case of pressure burner vaporizing tubes that operate at high temperatures. The usual test applied in this connection is the corrosion (copper strip) test (ASTM D-130, ASTM D-849, IP 154).

The copper strip test methods are used to determine the corrosiveness to copper of diesel fuel and are a measure of the relative degree of corrosivity of diesel fuel. Most sulfur compounds in petroleum are removed during refining. However, some residual sulfur compounds can have a corroding action on various metals, and the effect is dependent on the types of sulfur compounds present. One method (ASTM D-130, IP 154) uses a polished copper strip immersed in a given quantity of sample and heated at a temperature for a time period characteristic of the material being tested. At the end of this period the copper strip is removed, washed, and compared with the copper strip corrosion standards (ASTM, 2000). This is a pass/fail test. In another method (ASTM D-849) a polished copper strip is immersed in 200 ml of specimen in a flask with a condenser and placed in boiling water for 30 min. At the end of this period, the copper strip is removed and compared with the ASTM copper strip corrosion standards. This is also a pass/fail test.

Nitrogen compounds in diesel fuel and middle distillates can be selectively detected by chemiluminescence. Individual nitrogen compounds can be detected down to 100 ppb nitrogen.

Sulfur can cause wear, resulting from the corrosive nature of its combustion by -products and from an increase in the amount of deposits in the combustion chamber and on the pistons. The sulfur content of a diesel fuel (ASTM D-129, ASTM D-1266, ASTM D-l551, ASTM D-1552, ASTM D-2622, ASTM D-4294, IP 61, IP 63) depends on the origin of the crude oil from which it is made and on the refining methods. Sulfur can be present

in a number of forms, for example, as mercaptans, sulfides, disulfides, or heterocyclic compounds such as thiophenes, all of which will affect wear and deposits.

Sulfur is measured on the basis of both quantity and potential corrosivity. The quantitative measurements can be made by means of a combustion bomb (ASTM D-129, IP 61). The measurement of potential corrosivity can be determined by means of a copper strip procedure (ASTM D-l3, IP 154). The quantitative determination is an indication of the corrosive tendencies of the fuel combustion products, whereas the potential corrosivity indicates the extent of corrosion to be anticipated from the unburned fuel, particularly in the fuel injection system.

In gas turbine fuel, sulfur compounds (ASTM D-2880; notably hydrogen sulfide, elemental sulfur, and polysulfides) can be corrosive (ASTM D-130, IP 30) in the fuel handling systems and mercaptans can attack any elastomers present. Thus mercaptan sulfur content (ASTM D-235, ASTM D-3227, IP 30, IP 104) is limited to low levels because of objectionable odor, adverse effects on certain fuel system elastomers, and corrosiveness toward fuel system metals.

8.3.9. Density (Specific Gravity)

Density (or specific gravity) is an indication of the density or weight per unit volume of the diesel fuel. The principal use of specific gravity (ASTM D-l298, IP 160) is to convert weights of oil to volumes or volumes to weights. Specific gravity also is required when calculating the volume of petroleum or a petroleum product at a temperature different from that at which the original volume was measured. Although specific gravity by itself is not a significant measure of quality, it may give useful information when considered with other tests. For a given volatility range, high specific gravity is associated with aromatic or naphthenic hydrocarbons and low specific gravity with paraffinic hydrocarbons. The heat energy potentially available from the fuel decreases with an increase in density or specific gravity.

API gravity (ASTM D-1298, IP 160) is an arbitrary figure related to the specific gravity in accordance with the following formula:

$$°\text{API} = 141.5/(\text{specific gravity @ } 60/60°\text{F})/131.5$$

When a fuel requires centrifuging, density is a critical property and as the density of the fuel approaches the density of water (API gravity = 10°C) the efficiency of centrifuging decreases (ASTM D-2069). When separation of water from the fuel is not required, density is not a significant measure of fuel quality but it may give useful information when used in conjunction with other tests.

For example, for a given volatility range, high specific gravity is associated with aromatic or naphthenic hydrocarbons and low specific gravity with paraffinic hydrocarbons. Furthermore, calorific value (heat of combustion) decreases with an increase in density or specific gravity. However, calorific value expressed per volume of fuel increases with an increase in density or specific gravity.

8.3.10. Diesel Index

The diesel index is derived from the API gravity and aniline point (ASTM D-611, IP 2), the lowest temperature at which the fuel is completely miscible with an equal volume of aniline:

$$\text{diesel index} = \text{aniline point } (^\circ\text{F}) \times \text{API gravity}/100$$

The above equation is seldom used because the results can be misleading, especially when applied to blended fuels.

8.3.11. Flash Point

The flash point of a diesel fuel is the temperature to which the fuel must be heated to produce an ignitable vapor-air mixture above the liquid fuel when exposed to an open flame. The flash point test is a guide to the fire hazard associated with the use of the fuel and can be determined by several test methods, but the results are not always strictly comparable.

The minimum flash point is usually defined by the Abel method (IP 170), although the Pensky–Martens method (ASTM D-93, IP 34) may also be specified. The TAG method (ASTM D-56) is used for both the minimum and maximum limits, whereas certain military specifications also give minimum limits by the Pensky–Martens method (ASTM D-93, IP 34). The Abel method (IP 170) can give results up to 2–3°C (3–5°F) lower than the TAG method (ASTM D-56).

Similarly, for diesel fuel the flash point is a guide to the fire hazard associated with the fuel and can be determined by the same test methods as noted above (ASTM D-56, ASTM D-93, ASTM D-3828, IP 34, IP 170, IP 303).

It should be noted that the various flash point methods can yield different numerical results, and in the case of the two most commonly used methods (Abel and TAG) it has been found that the former (IP 170) can give results up to 1–2°C lower than the latter method (ASTM D-56). Setaflash (ASTM D-3828, IP 303) results are generally very close to Abel values.

In practice, flash point is important primarily for fuel handling. A flash point that is too low will cause fuel to be a fire hazard, subject to flashing

and possible continued ignition and explosion. In addition, a low flash point may indicate contamination by more volatile and explosive fuels, such as gasoline.

8.3.12. Freezing Point

Three test methods are available for determination of the freezing point. All three methods have been found to give equivalent results. However, when a specification calls for a specific test, only that test must be used.

In the first test (ASTM D-2386, IP 16), a measured fuel sample is placed in a jacketed sample tube also holding a thermometer and a stirrer. The tube is placed in a vacuum flask containing the cooling medium. Various coolants used are acetone, methyl alcohol, ethyl alcohol, or isopropyl alcohol, solid carbon dioxide, or liquid nitrogen. As the sample cools, it is continuously stirred. The temperature at which the hydrocarbon crystals appear is recorded. The jacketed sample is removed from the coolant and allowed to warm, under continuous stirring. The temperature at which the crystals completely disappear is recorded.

In the second test (ASTM D-5901, IP 434), an automated optical method is used for the temperature range to –70°C (–94°F). In this method, a 25-min portion of the fuel is placed in a test chamber that is cooled while continuously being stirred and monitored by an optical system. The temperature of the specimen is measured with an electronic measuring device, and the temperatures when crystals first appear and then, on warming, disappear are recorded.

In the third method (ASTM D-5972, IP 435), an automated phase transition method is used in the temperature range –80 to 20°C (–112°F to 68°F). In this test, a specimen is cooled at a rate of 15 ± 5°C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an array of optical detectors for the first formation of solid hydrocarbon crystals. After that the specimen is warmed at the rate of 10 ± 0.5°C/min until all crystals return to the liquid phase, and that temperature is also recorded.

The *freezing point* should not be confused with the *pour point*, which is an index of the lowest temperature at which the crude oil will flow under specified conditions.

An analogous property, the *cold filter plugging point* is suitable for estimating the lowest temperature at which diesel fuel will give trouble-free flow in certain fuel systems (ASTM D-6371, IP 309). In this test, either manual or automated apparatus may be used, which is cooled under specified conditions and, at intervals of 1°C, sample is drawn into a pipette under a controlled vacuum through a standardized wire mesh filter. As the sample continues to cool, the procedure is repeated for each 1°C below the first

test temperature. The testing is continued until the amount of wax crystals that have separated out of the solution is sufficient to stop or slow down the flow so that the time taken to fill the pipette exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the *cold filter plugging point*.

Alternatively, low-temperature flow test (ASTM D-4539) results are indicative of the low-temperature flow performance of fuel in some diesel vehicles. This test method is especially useful for the evaluation of fuels containing flow improver additives. In this test method, the temperature of a series of test specimens of fuel is lowered at a prescribed cooling rate. At the commencing temperature and at each 1°C interval thereafter, a separate specimen from the series is filtered through a 17-mm screen until a minimum low-temperature flow test pass temperature is obtained. The minimum low-temperature flow test pass temperature is the lowest temperature, expressed as a multiple of 1°C, at which a test specimen can be filtered in 60 s or less.

In another test (ASTM D-2068), which was originally designed for distillate fuel oil (Chapter 9), the filter-plugging tendency of diesel fuel can be determined by passing a sample at a constant flow rate (20 ml/min) through a glass fiber filter medium. The pressure drop across the filter is monitored during the passage of a fixed volume of test fuel. If a prescribed maximum pressure drop is reached before the total volume of fuel is filtered, the actual volume of fuel filtered at the time of maximum pressure drop is recorded. The apparatus is required to be calibrated at intervals.

8.3.13. Neutralization Number

Neutralization number (ASTM D-974, IP 139; IP 182) is a measure of the inorganic and total acidity of the unused fuel and indicates its tendency to corrode metals with which it may come into contact.

Corrosivity is also determined by a variety of copper corrosion text methods (ASTM D-130, ASTM D-849, IP 154).

8.3.14. Pour Point

The pour point (ASTM D-97, IP 15) of a fuel is an indication of the lowest temperature at which the fuel can be pumped. Pour points often occur 8–10°F below the cloud points, and differences of 15–20°F are not uncommon. Fuels, and in particular those fuels that contain wax, will in some circumstances flow below their tested pour point. However, the pour point does give a useful guide to the lowest temperature to which a fuel can be cooled without setting.

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. 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 characteristics. 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 operations. 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.

Sometimes additives are used to improve the low-temperature fluidity of diesel fuels. Such additives usually work by modifying the wax crystals so that they are less likely to form a rigid structure. Thus, although there is no alteration of the cloud point, the pour point may be lowered dramatically. Unfortunately, the improvement in engine performance as a rule is less than the improvement in pour point. Consequently, the cloud and pour point temperatures cannot be used to indicate engine performance with any accuracy.

8.3.15. Stability

On leaving the refinery, the fuel will inevitably come into contact with air and water. If the fuel includes unstable components, which may be the case with fuels containing cracked products, storage in the presence of air can lead to the formation of gums and sediments. Instability can cause filter plugging, combustion chamber deposit formation, and

gumming or lacquering of injection system components with resultant sticking and wear.

An accelerated stability test (ASTM D-2274) is often applied to fuels to measure their stability. A sample of fuel is heated for a fixed period at a given temperature, sometimes in the presence of a catalyst metal, and the amount of sediment and gum formed is taken as a measure of the stability.

In addition, the extent of oxidation of diesel fuel is determined by measurement of the hydroperoxide number (ASTM D-6447) and the peroxide number (ASTM D-3703). Deterioration of diesel fuel results in the formation of the peroxides as well as other oxygen-containing compounds, and these numbers are indications of the quantity of oxidizing constituents present in the sample as determined by measurement of the compounds that will oxidize potassium iodide.

The determination of hydroperoxide number is significant because of the adverse effect of hydroperoxides on certain elastomers in the fuel systems. This method (ASTM D-6447) measures the same peroxide species, primarily the hydroperoxides in diesel fuel. This test method does not use the ozone-depleting substance 1,1,2-trichloro-1,2,2-trifluoroethane (ASTM D-3703) and is applicable to any water-insoluble, organic fluid, particularly gasoline, kerosene, and diesel fuel. In this method, a quantity of sample is contacted with aqueous potassium iodide (KI) solution in the presence of acid. The hydroperoxides present are reduced by potassium iodide, liberating an equivalent amount of iodine, which is quantified by voltammetric analysis.

The determination of peroxide number of diesel fuel is important because of the adverse effects of peroxides on certain elastomers in the fuel system. In the test, the sample is dissolved (unlike ASTM D-6447) in 1,1,2-trichloro-l,2,2-trifluoroethane and is contacted within an aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide whereupon an equivalent amount of iodine is released that is titrated with standard sodium thiosulfate solution and a starch indicator.

Other tests for storage stability include determination of color formation and sediment (ASTM D-4625, ASTM D-5304) in which reactivity to oxygen at high temperatures is determined by the amount of sediment formation as well as any color changes.

8.3.16. Viscosity

Viscosity (ASTM D-445, IP 71) is a measure of the resistance to flow by a liquid and usually is measured by recording the time required for a given volume of fuel at a constant temperature to flow through a small orifice of standard dimensions. The viscosity of diesel fuel is important primarily

because of its effect on the handling of the fuel by the pump and injector system.

Fuel viscosity also exerts a strong influence on the shape of the fuel spray insofar as a high viscosity can result in poor atomization, large droplets, and high spray jet penetration. The jet tends to be almost a solid stream instead of forming a spray pattern of small droplets. As a result, the fuel is not distributed in, or mixed with, the air required for burning. Poor combustion is a result, accompanied by loss of power and economy. Moreover, and particularly in the smaller engines, the overly penetrating fuel stream can impinge upon the cylinder walls, thereby washing away the lubricating oil film and causing dilution of the crankcase oil. Such a condition contributes to excessive wear. On the other hand, fuels with a low viscosity can produce a spray that is too soft and thus does not penetrate sufficiently. Combustion is impaired, and power output and economy are decreased.

Fuel viscosities for high-speed engines range from 32 SUS to 45 SUS (2 cSt to 6 cSt) at 37.8°C (100°F). Usually the lower viscosity limit is established to prevent leakage in worn fuel injection equipment as well as to supply lubrication for injection system components in certain types of engines. During operation at low atmospheric temperature, the viscosity limit sometimes is reduced to 30 SUS (4 cSt) at 100°F to obtain increased volatility and sufficiently low pour point. Fuels having viscosities greater than 45 SUS (6 cSt) usually are limited in application to the slower-speed engines. The very viscous fuels, such as are often used in large stationary and marine engines, usually require preheating for proper pumping, injection, and atomization.

8.3.17. Volatility

Distillation (or volatility) characteristics of a diesel fuel exert a great influence on its performance, particularly in medium- and high-speed engines. Distillation characteristics are measured with a procedure (ASTM D-86, IP 123) in which a sample of the fuel is distilled and the vapor temperatures are recorded for the percentages of evaporation or distillation throughout the range. Other procedures are also available that are applicable to kerosene (Chapter 7).

The volatility requirement of diesel fuel varies with engine speed, size and design. However, fuels having too low volatility tend to reduce power output and fuel economy through poor atomization, and those having too high volatility may reduce power output and fuel economy through vapor lock in the fuel system or inadequate droplet penetration from the nozzle. In general, the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content, or viscosity of the fuel. If the 10% point is too high, poor starting may result. An

excessive boiling range from 10% to 50% evaporated may increase warm-up time. A low 50% point is desirable in preventing smoke and odor. Low 90% and end points tend to ensure low carbon residuals and minimum crankcase dilution.

The temperature for 50% evaporated, known as the mid-boiling point, usually is taken as an overall indication of the fuel distillation characteristics where a single numerical value is used alone. For example, in high-speed engines, a 50% point above 575°F (302°C) probably would cause smoke formation, give rise to objectionable odor, cause lubricating oil contamination, and promote engine deposits. At the other extreme, a fuel with excessively low 50% point would have too low a viscosity and too low a heat content per unit volume. Thus a 50% point in the range of 450–535 F (232–280°C) is most desirable for the majority of automotive-type diesel engines. This average range usually is raised to a higher temperature spread for larger, slower-speed engines.

The vapor pressure of diesel fuel at various vapor-to-liquid ratios is an important physical property for shipping, storage, and use. Although determining the volatility of diesel fuel is usually accomplished through a boiling range distribution (ASTM D-86, IP 123), determination of the Reid vapor pressure (ASTM D-323, IP 69) can also be used along with several other methods (ASTM D-5190, ASTM D-5482, ASTM D-6378).

8.3.18. Water and Sediment

Water can contribute to filter blocking and cause corrosion of the injection system components. In addition to clogging of the filters, sediment can cause wear and create deposits both in the injection system and in the engine itself. Thus one of the most important characteristics of a diesel fuel, the water and sediment content (ASTM D-1796, IP 75), is the result of handling and storage practices from the time the fuel leaves the refinery until the time it is delivered to the engine injection system.

Instability and resultant degradation of the fuel in contact with air contribute to the formation of organic sediment, particularly during storage and handling at elevated temperatures. Sediment generally consists of carbonaceous material, metals, or other inorganic matter. There are several causes of this type of contamination: (1) rust or dirt present in tanks and lines, (2) dirt introduced through careless handling practices, and (3) dirt present in the air breathed into the storage facilities with fluctuating atmospheric temperature.

Sediment can be determined individually (ASTM D-2276, ASTM D-6217) or by a test method that determines water simultaneously (ASTM D-2709. In the test method, a sample is centrifuged at a rcf of 800 for 10 min at 21–32°C in a centrifuge tube readable to 0.005 ml and measurable to

0.01 ml. After centrifugation, the volume of water and sediment that has settled into the tip of the centrifuge tube is read to the nearest 0.005 ml.

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CHAPTER

9

DISTILLATE FUEL OIL

9.1. INTRODUCTION

Most petroleum products can be used as fuels, but the term *fuel oil*, if used without qualification, may be interpreted differently depending on the context. However, because fuel oils are complex mixtures of hydrocarbons, they cannot be rigidly classified or defined precisely by chemical formulae or definite physical properties. The arbitrary division or classification of fuel oils is based more on their application than on their chemical or physical properties. However, two broad classifications are generally recognized: (1) *distillate fuel oil* and (2) *residual fuel oil* (Gruse and Stevens, 1960; Guthrie, 1967; Kite and Pegg, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Hemighaus, 1998; Warne, 1998; Speight, 1999; Charlot, and Claus, 2000; Heinrich and Duée, 2000). This terminology is used in the present work.

The conventional description of "fuel oil" is generally associated with the black, viscous residual material remaining as the result of refinery distillation of crude oil either alone or as a blend with light components, which is used for steam generation and various industrial processes. The term is sometimes used to refer to the light, amber-colored middle distillates or gas oils that are distinguished from the residual fuel oil by being characterized as distillate fuel oil (ASTM D-396). In this specification the No. 1 grade fuel oil is a kerosene type used in vaporizing pot-type burners whereas the No. 2 fuel is a distillate oil (gas oil) used for general-purpose domestic heating. Kerosene may also be included in this definition, but it is described elsewhere in this text.

Distillate fuel oils are vaporized and condensed during a distillation process and thus have a definite boiling range and do not contain high-boiling oils or asphaltic components. The generally correspond to a light gas oil (Table 9.1, Fig. 9.1), but this correlation is not exact and can vary considerably. A fuel oil that contains any amount of the residue from crude distillation of thermal cracking is a residual fuel oil. The terms *distillate fuel oil*. and *residual fuel oil* are losing their significance, because fuel oils are now made for specific uses and may be either distillates or residuals or

Table 9.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

mixtures of the two. The terms *domestic fuel oil*, *diesel fuel oil*, and *heavy fuel oil* are more indicative of the uses of fuel oils.

Domestic fuel oil is fuel oil that is used primarily in the home. This category of fuel oil includes kerosene, stove oil, and furnace fuel oil; these are distillate fuel oils. Diesel fuel oil is also a distillate fuel oil, but residual oil has been successfully used to power marine diesel engines, and mixtures of distillate fuel oil and residual fuel oil have been used in locomotive diesel engines. Heavy fuel oils include a variety of oils ranging from distillates to residual oils that must be heated to 260°C (500°F) or more before they can be used. In general, heavy fuel oils consist of residual oils blended with distillates to suit specific needs. Included among heavy fuel oils are various industrial oils; when used to fuel ships, heavy fuel oils are called bunker oils.

Because the boiling ranges, sulfur contents, and other properties of even the same fraction vary from crude oil to crude oil and with the way the crude oil is processed, it is difficult to specify which fractions are blended to produce specific fuel oils. In general, however, furnace fuel oil is a blend of straight-run gas oil and cracked gas oil to produce a product boiling in the 175–345°C (350–650°F) range.

Heavy fuel oils usually contain cracked residua, reduced crude, or cracking coil heavy product that is mixed (cut back) to a specified viscosity with cracked gas oils and fractionator bottoms. For some industrial purposes in which flames or flue gases contact the product (ceramics, glass, heat treating, and open-hearth furnaces) fuel oils must be blended to contain

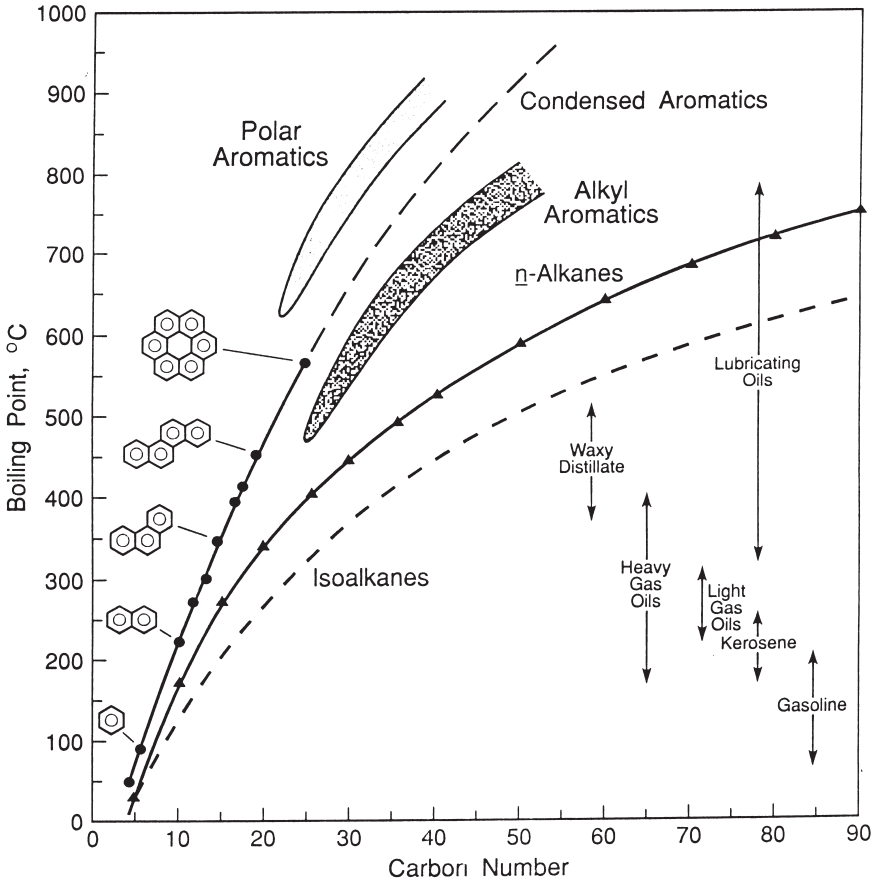

Figure 9.1. Boiling point and carbon number for various hydrocarbons and petroleum products

minimum sulfur contents, and hence low-sulfur residues are preferable for these fuels.

9.2. PRODUCTION AND PROPERTIES

Distillate fuel oils are petroleum fractions that have been vaporized and condensed. They are produced in the refinery by a distillation process in which petroleum is separated into its fractions according to their boiling range. Distillate fuel oils may be produced not only directly from crude oil (*straight run*) but also from subsequent refinery processes such as thermal

or catalytic cracking. Domestic heating oils and kerosene are examples of distillate fuel oils.

The manufacture of fuel oils at one time largely involved using what was left after removing desired products from crude petroleum. Now fuel oil manufacture is a complex matter of selecting and blending various petroleum fractions to meet definite specifications, and the production of a homogeneous, stable fuel oil requires experience backed by laboratory control.

The term *domestic heating oil* in the present context is applicable to the middle distillate or gas oil-type product used principally with atomizing burner-heating equipment. This material may consist of the straight-run gas oil from the distillation of the crude oil, which boils within the approximate temperature range of l60–370°C (320–700°F). Straight-run gas oil fraction is usually blended with the appropriate boiling-range material from catalytic cracking processing. The components are suitably treated before final blending, and additives may also be added to further assist in the stabilization of the finished product.

The quality and performance requirements for fuel oils differ widely, although general quality limitations for various fuel grades are used to serve as guides in the manufacture, sale, and purchase of the oils. These quality definitions are often referred to as *specifications* or *classifications*, but more precise specifications of quality requirements such as the vapor pressure (ASTM D-323) and metals content (ASTM D-5184, ASTM D-2788, ASTM D-4951, ASTM D-5185, ASTM D-5708, ASTM D-5863, IP 377) may be required for any given application (ASTM D-396).

9.3. TEST METHODS

Fuel oil, therefore, in its various categories has an extensive range of applications, and the choice of a standard procedure to be used for assessing or controlling product quality must, of necessity, depend on both the type of fuel and its ultimate use. But first, as for all petroleum analysis and testing, the importance of correct sampling of the fuel oil cannot be overemphasized, because no proper assessment of quality can be made unless the data are obtained on truly representative samples (ASTM D-270, IP 51).

9.3.1. Acidity

The presence of inorganic acids in distillate fuels, resulting from refinery treatment, is unlikely. However, some specifications for these fuels still include limiting clauses for total acidity and inorganic acidity as a check against possible corrosion of metal equipment in contact with the fuel. Inorganic acidity should in any case be entirely absent.

Acidity is determined through the *acid number*, which is the quantity of base, expressed in 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 basic buffer solution or a well-defined inflection point as specified in the test method. Test methods include potentiometric titration (ASTM D-66, IP 177) and indicator-indicator titration (ASTM D-974, IP 139) in addition to inorganic acidity (IP 182) and total acidity (IP 1) methods.

One test method (ASTM D-974) resolves constituents into groups having weak acid and strong acid ionization properties. However, oils such as fuel oil that are dark-colored oils, which cannot be analyzed by this test method because of obscurity of the color-indicator end point, should be analyzed by another test method (ASTM D-664, IP 177) This test method is used to determine the presence of those constituents that have weak acid properties and those constituents that have strong acid properties. It may be used to indicate relative changes that occur in an oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil. In the practice of this method, 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 by using a glass indicating electrode and a calomel reference electrode and the end points are taken at well-defined inflections in the resulting curve.

9.3.2. Ash Content

Ash is the organic matter-free (or carbonaceous matter free) residue that remains after combustion of a fuel oil at a specified high temperature (ASTM D-482, IP 4).

Depending on the use of the fuel, ash composition has a considerable bearing on whether or not detrimental effects will occur. However, distillate fuels tend to contain only negligible amounts of ash but pick up ash-forming constituents during transportation from the refinery. Water transportation, in particular, presents many opportunities for fuel oils to be contaminated with ash-forming contaminants (seawater, dirt, and scale rust).

Small amounts of unburnable material are found in fuel oil in the form of soluble metallic soaps and solids, and these materials are designated as ash, although "ash-forming constituents" is a more correct term. In the test for the quantitative determination of ash-forming constituents (ASTM D-482, IP 4), a small sample of fuel oil is burned in a weighed container until all of the combustible matter has been consumed, as indicated by the residue and container attaining a constant weight. The amount of unburnable residue is the ash yield, and it is reported as percent by weight of the sample.

The ash-forming constituents in distillate fuel (ASTM D 2880) are typically so low that they do not adversely affect gas turbine performance, unless such corrosive species as sodium, potassium, lead, or vanadium are present. However, there are recommendations for the storage and handling of these fuels (ASTM D-4418) to minimize potential contamination.

9.3.3. Calorific Value (Heat of Combustion)

Because the function of a fuel is to produce heat, the calorific or heating value (ASTM D-240, IP 12) is one of the important fuel properties and a knowledge of this value is necessary in obtaining information regarding the combustion efficiency and performance of all types of oil-burning equipment.

The determination is made in a bomb calorimeter under specified conditions, the oxygen in the bomb being saturated with water vapor before the ignition of the fuel so that the water formed during combustion is condensed. The calorific value so determined will include the latent heat of water at the test temperature and is known as the gross calorific value at constant volume. The corresponding net calorific value at constant pressure is obtained by deducting the latent heat of water formed during the burning of the hydrogen present in the fuel to produce water. The calorific value is usually expressed in British thermal units per pound (Btu/lb) or in calories per gram (c/g). In Europe the net calorific value is more often called for in calculations on burner efficiency because the water formed during combustion passes out as water vapor with the flue gases and hence its latent heat of condensation is not realized as useful heat. In the U.K. the gross calorific value is normally used for this purpose.

An alternative criterion of energy content is the *aniline gravity product* (AGP), which is related to calorific value (ASTM D-1405, IP 193). The aniline gravity product is the product of the API gravity (ASTM D-287, ASTM D-1298) and the aniline point of the fuel (ASTM D-611, IP 2). The aniline point is the lowest temperature at which the fuel is miscible with an equal volume of aniline and is inversely proportional to the aromatic content. The relationship between the aniline gravity product and the calorific value is given in the method. In another method (ASTM D-3338), the heat of combustion is calculated from the fuel density, the 10%, 50%, and 90% distillation temperatures, and the aromatic content. However, neither method is legally acceptable, and other methods (ASTM D-240, ASTM D-1655, ASTM D-4809) are preferred.

The aniline gravity product is not always suitable for determining the heat of combustion because of the difficulties that can be encountered in determining the aniline point of the fuel (ASTM D-611, IP 2). It is

possible to overcome the issue of color by use of a modification of the test procedure (method B, ASTM D-611, IP 2).

An alternate method of calculation of the calorific value, when an experimental determination is not available or cannot be made conveniently, involves an estimate of this property (ASTM D-6446). In this test method, the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the hydrogen content (ASTM D-1018, ASTM D-1217, ASTM D-1298, ASTM D-3701, ASTM D-4052, ASTM D-4808, ASTM D-5291, IP 160, IP 365), density (ASTM D-129, ASTM D-1250, ASTM D-1266, ASTM D-2622, ASTM D-3120, IP 61, IP 107), and sulfur content (ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 336, IP 373) of the sample are determined by experimental test methods, and the net heat of combustion is calculated with the values obtained by these test methods based on reported correlations.

9.3.4. Carbon Residue

The carbon residue of a petroleum product gives an indication of the propensity for that product to form a carbonaceous residue under thermal conditions. The carbonaceous residue is correctly referred to as the *carbon residue* but is also often referred to as *coke* or *thermal coke*.

The use of fuel oil (ASTM No. 2) for heating has resulted in the availability of different types of burners that are classified according to the manner in which the fuel oil is combusted. Any carbonaceous residue formed during the thermal decomposition of the fuel oil that is deposited in, or near, the inlet surface, reduces the fuel oil flow, with resultant loss in burner efficiency. Therefore, fuel oil should have low carbon-forming propensities. Other petroleum products that are lower boiling than distillate fuel oil do not usually reference the carbon residue in the specifications.

Thus assessing the carbon forming tendencies of the fuel oil is carried out with a carbon residue test. The test methods are (1) the Conradson carbon residue (ASTM D-189, IP 13), the Ramsbottom carbon residue (ASTM D-524, IP 14), and the microcarbon carbon residue (ASTM D-4530, IP 398). 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. For lower-boiling fuel oil, forming low yields of carbonaceous deposits, the carbon residue value is determined

on a residue (10% by weight of the fuel oil) obtained by means of an adaptation of the standard distillation procedure for gas oil (ASTM D-8, IP 123), so that the accuracy of the determination may be improved.

9.3.5. Cloud Point

Distillate fuel oil for heating installations is usually stored in outside tankage, and a knowledge of the lowest temperature at which the fuel can be transferred from tank to burner while avoiding line and filter blockage difficulties is necessary.

An indication of this temperature may be obtained from the cloud point (ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP 219) and pour point (ASTM D-97, IP 15). These test methods give, respectively, the temperature at which wax begins to crystallize out of the fuel and the temperature at which the wax structure has built up sufficiently to prevent the flow of oil. In these installations, a coarse filter is normally sited in the system near the tank outlet to remove large particles of extraneous matter; a fine filter is positioned near the burner to protect the pump.

As the temperature continues to decrease below the cloud point, the formation of wax crystals is accelerated. These crystals clog fuel filters and lines and thus reduce the supply of fuel to the burner. Because the cloud point is a higher temperature than the pour point (4 to 5°C/7 to 9°F, and even higher), the cloud point is often considered to be more important than the pour point in establishing distillate fuel oil specifications for cold weather usage. The temperature differential between cloud and pour point depends on the nature of the fuel components, but the use of wax crystal modifiers or pour depressants tends to accentuate these differences.

9.3.6. Composition

The chemical composition of fuel oil is extremely complex, and an extremely high number of compounds can be present through the hydrocarbon types, the range of isomeric hydrocarbons (Table 9.2), and the various types and isomers of heteroatom constituents. Therefore, it is not practical to perform individual compound analyses but it is often helpful to define the compounds present under broad classifications, such as aromatics, paraffins, naphthenes, and olefins.

Thus the first level of compositional information is group type totals as deduced by adsorption chromatography (ASTM D-1319, ASTM D-2007) or by emulsion chromatography (ASTM D-2549) to give volume percent saturates, olefins, and aromatics in materials that boil below 315°C (600°F). In addition, and depending on the characteristics of the fuel oil, gas chromatography can also be used for the quantitative determination of olefins

Table 9.2. Increase in Number of Isomers with Carbon Number

Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

(ASTM D-6296). Following from the chromatographic separation, compositional analysis of the fractions by a mass spectral Z series in which Z in the empirical formula C_nH_{2n+Z} is a measure of the hydrogen deficiency of the compound is also warranted (ASTM D-2425, ASTM D-2786, ASTM D-3239, ASTM D-6379).

One mass spectrometric method (ASTM D-2425) requires that the sample be separated into saturate and aromatic fractions before mass spectrometric analysis. This separation is standardized (ASTM D-2549). This separation is applicable to fuel only when it is possible to evaporate the solvent used in the separation without also losing the light ends of the jet fuel. Combined gas chromatography-mass spectrometry has been used to give similar group type results to ASTM D-2425 but without preseparation into saturates and aromatics. In addition, this method can give the Z series information by carbon number, showing how the composition changes with boiling point.

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined (ASTM D-5292). Results from this test are not equivalent to mass- or volume-percent aromatics determined by the chromatographic methods. The chromatographic methods determine the mass- or volume-percentage of molecules that have one or more aromatic rings. Any alkyl substituents on the rings contribute to the percentage of aromatics determined by chromatographic techniques. ASTM D-292 gives the mole percent of aromatic hydrogen or carbon atoms.

Correlative methods have long been used as a way of dealing with the complexity of petroleum fractions. Such methods include the use of viscosity-temperature charts (ASTM D-341), calculation of the viscosity index (ASTM D-2270), calculation of the viscosity gravity constant (ASTM D-2501), calculation of the true vapor pressure (ASTM D-2889), and estimation of the heat of combustion (ASTM D-3338).

Organic sulfur compounds (e.g., mercaptans, sulfides, polysulfides, thiophenes) are present in petroleum products to a greater or lesser extent depending on the crude oil origin and the refinery treatment. The sulfur content of fuel oil (ASTM D-396) can be determined by a variety of methods (ASTM D-129, ASTM D-1552, ASTM D-2622, ASTM D-4294, IP 61, IP 63), with mercaptan sulfur in cracked stocks being particularly necessary for evaluation (ASTM D-3227, IP 342).

Corrosion of heating equipment can occur if the sulfur oxides formed on combustion of fuel oil are allowed to condense in the presence of moisture on the cooler parts of the flue system. Corrosion of metal parts of the fuel system may also reflect the presence of corrosive sulfur components in the fuel. The corrosive tendencies of the fuel may be detected by the copper strip test (ASTM D-l30, ASTM D-849, IP 154), the effect of these sulfur compounds being indicated by discoloration of the copper strip.

Various standard procedures are available for the determination of the sulfur content of distillate fuels. In the lamp method (ASTM D-l26, IP 107), which is widely used, the product is burned completely in a small wick-fed lamp, the gases formed by combustion are absorbed in hydrogen peroxide solution, and the sulfur is subsequently determined as sulfate. Several rapid methods, including X-ray absorption and high-temperature combustion, for the determination of sulfur are also available.

In addition, excessive levels of hydrogen sulfide in the vapor phase above fuel oils in storage tanks may result in corrosion as well as being a health hazard. One method (ASTM D-5705) is available for the determination of hydrogen sulfide but has been criticized because the test conditions do not simulate the vapor phase of a fuel storage tank. A second method (ASTM D-6021) that is believed to be a more accurate simulation of the conditions in a fuel oil storage tank is available. In this method, a sample of the fuel oil is placed in a headspace vial and heated in an oven at 60°C (140°F) for more than 5 min but less than 15 min. The headspace gas is sampled and injected into an apparatus capable of measuring hydrogen sulfide in the gaseous sample either by the lead acetate method (ASTM D-4084, ASTM D-4323) or by the chemiluminescence method (ASTM D-5504).

Nitrogen can be determined by elemental analysis (ASTM D-3228, ASTM D-5291, ASTM D-5762). Nitrogen compounds in middle distillates can be selectively detected by chemiluminescence (ASTM D-4629). Individual nitrogen compounds can be detected down to 100 ppb nitrogen.

9.3.7. Density (Specific Gravity)

The density (specific gravity) of fuel oil is an index of the weight of a measured volume of the product (ASTM D-287, ASTM D- D 1250, ASTM D-1298, ASTM D-1480, ASTM D-1481, ASTM D-4052, IP 160, IP 192, IP 200, IP 365).

The density is the mass (weight *in vacuo*) of a unit volume of fuel oil at any given temperature (ASTM D-1298, IP 160). On the other hand, the specific gravity of a fuel oil is the ratio of the weight of a given volume of the material at a temperature of 15.6°C (60°F) to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air.

The API gravity (ASTM D-1298, IP 160) is an arbitrary figure related to the specific gravity:

$$°\text{API} = 141.5/(\text{specific gravity @ } 60/60°\text{F})/131.5$$

9.3.8. Flash Point

The *flash point* is a measure of the temperature to which fuel oil must be heated to produce an ignitable vapor-air mixture above the liquid fuel when exposed to an open flame. Following from this, the *fire point* of a fuel is the temperature at which an oil in an open container gives off vapor at a sufficient rate to continue to burn after a flame is applied.

Thus the flash point is used primarily as an index of fire hazards. Consequently, most industry specifications or classifications place limits on the flash point to ensure compliance with fire regulations, insurance, and legal requirements because it is essential that the fuel is safe to transport and store. Generally, because of its distillation characteristics, fuel oil should not contain any volatile or *flashable* constituents. Nevertheless, the occasion might arise when application of test methods to determine the flash point might be applicable.

The test method for determination of the flash point by Pensky–Martens closed tester (ASTM D-93, IP 34) and the test method for determining flash point by the tag closed tester (ASTM D-56) are employed for fuel oil.

9.3.9. Metallic Constituents

Metals in fuel oil can seriously affect the use and outcome of fuel oil systems. Even trace amounts of metals can be deleterious to fuel oil use. Hence, it is important to have test methods that can determine metals, both at trace levels and at major concentrations. Metallic constituents in fuel oil can be determined by several methods including atomic absorption

spectrophotometry (ASTM D-2788, ASTM D-5863, ASTM D-5863, IP 285, IP 288, IP 465), X-ray fluorescence spectrometry (ASTM D-4927, IP 407), wavelength-dispersive X-ray fluorescence spectrometry (ASTM D-6443, IP 433), and inductively coupled plasma emission spectrometry (ICPAES) (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.

9.3.10. Pour Point

The *pour point* (ASTM D-97, IP 15) is the lowest temperature at which the fuel oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where a petroleum product, depending on its thermal history, might appear in the liquid as well as the solid state. 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. The *pour point* should not be confused with the *freezing point*, which is an index of the lowest temperature at which the crude oil will flow under specified conditions. Test methods (ASTM D-2386, ASTM D-5901, ASTM D-5972, IP 434, IP 435) for the freezing point are not usually applicable to fuel oil but are more applicable to diesel fuel and aviation fuel.

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 petroleum and petroleum products down to –36°C (–33°F). 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 characteristics. 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 fuel line operations. 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.

Although the pour point test is still included in many specifications, it is not designated for high-boiling fuel oil (ASTM D 396). In fact, although the failure to flow at the pour point normally is attributed to the separation of wax from the fuel oil (in the case of waxy crude oil precursors), it also can be due to the effect of the viscosity of the fuel oil (in the case of naphthenic crude oil precursors). In addition, the pour point of fuel oil may be influenced by the previous thermal history of the fuel oil. Thus the usefulness of the pour point test in relation to fuel oil, especially residual fuel oil, may be open to question.

Perhaps a more important test is the test the *cold filter plugging point*. The cold filter plugging point is the lowest temperature at which fuel oil will give trouble-free flow (ASTM D-6371, IP 309). In this test, either a manual or automated apparatus may be used and the sample is cooled under specified conditions, and at intervals of 1°C, is drawn into a pipette under a controlled vacuum through a standardized wire mesh filter. As the sample continues to cool, the procedure is repeated for each 1°C below the first test temperature. The testing is continued until the amount of wax crystals that have separated out of the solution is sufficient to stop or slow down the flow so that the time taken to fill the pipette exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the *cold filter plugging point*.

Alternatively, in the low-temperature flow test involving determination of the filterability of fuel oil (ASTM D-4539, ASTM D-6426) the results are indicative of the low-temperature flow performance of distillate fuel oil. Both tests are useful for the evaluation of fuel oil containing flow improver additives. In either test method, the temperature of a series of test specimens of fuel is lowered at a prescribed cooling rate. At the commencing temperature and at each 1°C interval thereafter, a separate specimen from the series is filtered through a 17-mm screen until a minimum low-temperature flow test pass temperature is obtained. The minimum low-temperature flow test pass temperature is the lowest temperature, expressed as a multiple of 1°C, at which a test specimen can be filtered in 60 s or less.

In another test (ASTM D-2068), the filter plugging tendency of distillate fuel oil can be determined by passing a sample at a constant flow rate (20 ml/min) through a glass fiber filter medium. The pressure drop across the filter is monitored during the passage of a fixed volume of test fuel. If a prescribed maximum pressure drop is reached before the total volume of fuel is filtered, the actual volume of fuel filtered at the time of maximum pressure drop is recorded. The apparatus is required to be calibrated at intervals.

9.3.11. Stability

Fuel oil must be capable of storage for many months without significant change and should not break down to form gum or insoluble sediments or darken in color (ASTM D-156, ASTM D-381, ASTM D-1209, ASTM D-1500, ASTM D-1544, IP 131). In other words, fuel oil must be stable.

The extent of fuel oil oxidation is determined by measurement of the hydroperoxide number (ASTM D-6447) and the peroxide number (ASTM D-3703). Deterioration of fuel oil results in the formation of peroxides as well as other oxygen-containing compounds, and these numbers are indications of the quantity of oxidizing constituents present in the sample as determined by measurement of the compounds that will oxidize potassium iodide.

The determination of hydroperoxide number (ASTM D-6447) does not use the ozone-depleting substance 1,1,2-trichloro-1,2,2-trifluoroethane that is used for determination of the peroxide number (ASTM D-3703). In this method, a quantity of sample is contacted with aqueous potassium iodide (KI) solution in the presence of acid. The hydroperoxides present are reduced by potassium iodide, liberating an equivalent amount of iodine, which is quantified by voltammetric analysis.

The determination of peroxide number (ASTM D-3703) involves dissolution of the sample in 1,1,2-trichloro-l,2,2-trifluoroethane, and the solution is contacted with an aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide, whereupon an equivalent amount of iodine is released that is titrated with standard sodium thiosulfate solution and a starch indicator.

Other tests for storage stability include determination of color formation and sediment (ASTM D-473, ASTM D-2273, ASTM D-3241, ASTM D-4625, ASTM D-4870, ASTM D-5304, IP 53, IP 323), in which reactivity to oxygen at high temperatures is determined by the amount of sediment formation as well as any color changes.

Straight-run fuel oil fractions from the same crude oil normally are stable and mutually compatible. However, fuel oil produced from the thermal cracking and visbreaking operations may be stable by themselves but can be unstable or incompatible if blended with straight-run fuels and vice versa. Furthermore, asphaltic deposition may result from the mixing of (distillate and residual) fuel oils of different origin and treatment, each of which

may be perfectly satisfactory when used alone. Such fuels are said to be incompatible, and a spot test (ASTM D-470) is available for determining the stability and compatibility of fuel oils. Therefore, test procedures are necessary to predict fuel stability and to ensure a satisfactory level of performance by the fuel oil.

In addition, thermal treatment may cause the formation of asphaltene-type material in fuel oil. 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 is an indicator of the amount of carbonaceous residue that can be expected during thermal use or further processing (ASTM D-189, ASTM D-524, ASTM D4530, IP 13, IP 14, IP 398) (Speight, 1999; Speight, 2001; Speight and Ozum 2002).

In any of the methods for the determination of the asphaltene content (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143), 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 by weight 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 by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in a 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 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 precipitating number. In the test, 10 ml of sample is mixed with 90 ml of ASTM precipitation naphtha (that 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.

Another method, not specifically described as an asphaltene separation method, is designed to remove pentane-insoluble constituents by mem-

brane filtration (ASTM D-4055). In this method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer any particulates onto the filter, after which the filter (with particulates) is dried and weighed to give the pentane-insoluble constituents as a percentage by weight of the sample. Particulates can also be determined by membrane filtration (ASTM D-2276, ASTM D-5452, ASTM D-6217, IP 415).

The storage stability of fuel oil may also be influenced by the crude oil origin, hydrocarbon composition, and refinery treatment (especially if unsaturated constituents are present). Fuel oil containing unsaturated hydrocarbons has a greater tendency to form sediment on aging than the straight-run fuel oils. Unsaturated hydrocarbon constituents can be determined by the bromine number. (ASTM D-1159, ASTM D-2710, IP 130).

The bromine number is the number of grams of bromine that will react with 100 g of the sample under the test conditions. The magnitude of the bromine number is an indication of the quantity of bromine-reactive constituents and is not an identification of constituents. It is used as a measure of aliphatic unsaturation in petroleum samples and of the percentage of olefins in petroleum distillates boiling up to approximately 315°C (600°F). In this test, a known weight of the sample dissolved in a specified solvent maintained at 0–5°C (32–41°F) is titrated with standard bromide-bromate solution. Determination of the end point is method- and sample dependent, being influenced by color.

The presence of reactive compounds of sulfur (e.g., thiophenes), nitrogen (pyrroles), and oxygen is also considered to contribute to fuel instability (Mushrush and Speight, 1995; Mushrush and Speight, 1998a; Mushrush and Speight, 1998b; Mushrush et al., 1999).

To ensure a product of satisfactory stability, test procedures are necessary to predict this aspect of quality control. One particular method (ASTM D-2274) uses short-term, high temperature procedures that are generally preferred to long-term, lower-temperature conditions. Although the accuracy of these empirical tests leaves much to be desired they do provide, with some background knowledge of the fuel, useful data relating to the fuel's storage stability characteristics. And it is not often acknowledged that higher temperatures can, and often do, change the chemistry of the aging process, thereby leaving much open to speculation.

9.3.12. Viscosity

The viscosity of a fluid is a measure of its resistance to flow and is expressed as Saybolt Universal seconds (SUS), Saybolt Furol seconds (SFS), or centistokes (cSt, kinematic viscosity). Viscosity is one of the more important

heating oil characteristics because it is indicative of the rate at which the oil will flow in fuel systems and the ease with which it can be atomized in a given type of burner.

For the determination of the viscosity of petroleum products various procedures, such as Saybolt (ASTM D-88) and Engler, are available and have been in use for many years, all being of an empirical nature, measuring the time taken in seconds for a given volume of fuel to flow through an orifice of specified dimensions.

The use of these empirical procedures is being superseded by the more precise kinematic viscosity method (ASTM D-445, IP 71), in which a fixed volume of fuel flows through the capillary of a calibrated glass capillary viscometer under an accurately reproducible head and at a closely controlled temperature. The result is obtained from the product of the time taken for the fuel to flow between two etched marks on the capillary tube and the calibration factor of the viscometer and is reported in centistokes. Because the viscosity decreases with increasing temperature the temperature of test must also be reported if the viscosity value is to have any significance. For distillate fuel oils the usual test temperature is 38°C (100°F).

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 and petroleum products between 40 and 100°C (104 and 212°F). For samples 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.

9.3.13. Volatility

The volatility of fuel oil must be uniform, from batch to batch, if too-frequent resetting of burner controls is to be avoided and if maximum performance and efficiency are to be maintained. Information regarding the volatility and the proportion of fuel vaporized at any one temperature may be obtained from the standard distillation procedure (ASTM D-86, IP 123). The distillation test is significant for the distillate fuels because it is essential that the fuels contain sufficient volatile components to ensure that ignition and flame stability can be accomplished easily.

The distillation procedure (ASTM D 86, IP 123) measures the amount of liquid vaporized and subsequently condensed as the temperature of the fuel in the distillation flask is raised at a prescribed rate. A record is made of the volume of distillate collected at specified temperatures or, conversely, the temperature at each increment of volume distilled (usually 10% increments). The temperature at which the first drop of condensate is collected is called the *initial boiling point*. The *end point* usually is the highest

temperature recorded as the bottom of the flask becomes dry. If the sample is heated above 370°C (698°F), cracking occurs and the data are erroneous. The test usually is stopped when this point is reached. Some distillations may be run under reduced pressure (10 mmHg) to avoid cracking (ASTM D-1160). Under these conditions, fuel oil constituents may be distilled up to temperatures equivalent to 510°C (950°F) at atmospheric pressure.

Specifications for fuel oil may include limits on the temperatures at which 10% and 90% of the fuel are distilled by the standard procedure (ASTM D-396). For kerosene-type fuel oil (ASTM D-1) these values control the volatility at both ends of the distillation range, whereas for gas oil (ASTM D-1, ASTM D-2), where the front-end volatility is not so critical, only the 90% distillation temperature is normally specified. This ensures that high-boiling-point components, which are less likely to burn and which can cause carbon deposition, are excluded from the fuel.

One particular method is specifically designed for a high-boiling petroleum fraction having an initial boiling point greater than 150°C (300°F) (ASTM D-5236). The method consists of a pot still with a low-pressure drop entrainment separator operated under total takeoff conditions. The maximum achievable temperature, up to 565°C (1050°F), is dependent on the heat tolerance of the charge, but for distillate fuel oil the need to approach the maximum temperature is unnecessary. In this method, a weighed volume of the sample is distilled at pressures between 0.1 and 50 mmHg at specified distillation rates. Fractions are taken at preselected temperatures with records being made of the vapor temperature, the operating pressure, and any other variables deemed necessary. From the mass and density of each fraction distillation. yields by mass and volume can be calculated.

The boiling range distribution of certain fuel oils can be determined by gas chromatography (ASTM D-6352). This test method is applicable to petroleum distillate fractions with an initial boiling point of <700°C (<1292°F) at atmospheric pressure. The test method is not applicable to products containing low-molecular-weight components, for example, naphtha, reformate, gasoline, residuum, and petroleum itself, and should not be used for materials that contain heterogeneous components such as alcohols, ethers, esters, or acids or residue. In the method, a nonpolar open tubular capillary gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. A sample aliquot diluted with a viscosity-reducing solvent is introduced into the chromatographic system, and the column oven temperature is raised at a specified linear rate to effect separation of the hydrocarbon components. Retention times of known normal paraffin hydrocarbons spanning the scope of the test method are used for normalizing the retention times of the constituents of the fuel oil.

9.3.14. Water and Sediment

Considerable importance is attached to the presence of water or sediment in fuel oil because they lead to difficulties in use such as corrosion of equipment and blockages in fuel lines.

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 the equipment, corrosion due to chloride decomposition, and a lowering of residual fuel quality.

In any form, water and sediment are highly undesirable in fuel oil 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 examinations of quality.

The Karl Fischer test method (ASTM D-1364, ASTM D-6304) covers the direct determination of water in petroleum products. 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 can be determined simultaneously (ASTM D-96, ASTM D-4007, IP 359) by the centrifuge method. Known volumes of the fuel oil 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 fuel oil 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.

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CHAPTER

10

RESIDUAL FUEL OIL

10.1. INTRODUCTION

The term *fuel oil* is applied not only to distillate products (*distillate fuel oil*, Chapter 9) but also to residual material, which is distinguished from distillate type fuel oil by boiling range and, hence, is referred to as *residual fuel oil* (ASTM D-396).

Thus *residual fuel oil* is fuel oil that is manufactured from the distillation residuum, and the term includes all residual fuel oils, including fuel oil obtained by visbreaking as well as by blending residual products from other operations (Gruse and Stevens, 1960; Guthrie, 1967; Kite and Pegg, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Hemighaus, 1998; Warne, 1998; Speight, 1999; Charlot and Claus, 2000; Heinrich and Duée, 2000). The various grades of heavy fuel oils are produced to meet rigid specifications to ensure suitability for their intended purpose.

Detailed analysis of residual products, such as residual fuel oil, is more complex than the analysis of lower-molecular-weight liquid products. As with other products, there are a variety of physical property measurements that are required to determine whether the residual fuel oil meets specification, but the range of molecular types present in petroleum products increases significantly with an increase in the molecular weight (i.e., an increase in the number of carbon atoms per molecule). Therefore, characterization measurements or studies cannot, and do not, focus on the identification of specific molecular structures. The focus tends to be on molecular classes (paraffins, naphthenes, aromatics, polycyclic compounds, and polar compounds).

Several tests that are usually applied to the lower-molecular-weight colorless (or light-colored) products are not applied to residual fuel oil. For example, test methods such as those designed for the determination of the aniline point (or mixed aniline point) (ASTM D-611, IP 2) and the cloud point (ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773) can suffer from visibility effects because of the color of the fuel oil.

10.2. PRODUCTION AND PROPERTIES

Visbreaking (viscosity reduction, viscosity breaking) is the most widely used process for the production of residual fuel oil. It is a relatively mild thermal cracking operation used to reduce the viscosity of residua (Bland and Davidson, 1967; Ballard et al., 1992; Speight and Ozum, 2002). Residua are sometimes blended with lighter heating oils to produce residual fuel oil of acceptable viscosity. By reducing the viscosity of the nonvolatile fraction, visbreaking reduces the amount of the more valuable light heating oil that is required for blending to meet the fuel oil specifications. The process is also used to reduce the pour point of a waxy residue.

In the visbreaking process, a residuum is passed through a furnace where it is heated to a temperature of approximately 480°C (895°F) under an outlet pressure of about 100 psi (Speight, 1999; Speight and Ozum, 2002). The heating coils in the furnace are arranged to provide a soaking section of low heat density, where the charge remains until the visbreaking reactions are completed. The cracked products are then passed into a flash distillation chamber. The overhead material from this chamber is then fractionated to produce a low-quality gasoline as an overhead product and light gas oil as bottoms. The liquid products from the flash chamber are cooled with a gas oil flux and then sent to a vacuum fractionator. This yields a heavy gas oil distillate and a residuum of reduced viscosity. A quench oil may also be used to terminate the reactions. A 5–10% by weight or by volume conversion of atmospheric residua to naphtha is usually sufficient to afford at least an approximate fivefold reduction in viscosity. Reduction in viscosity is also accompanied by a reduction in the pour point.

The reduction in viscosity of residua tends to reach a limiting value with conversion, although the total product viscosity can continue to decrease but other properties will be affected. Sediment (which is predominantly organic but may contain some mineral matter) may also form—a crucial property for residual fuel oil—and conditions should be chosen so that sediment formation is minimal, if it occurs at all. When shipment of the visbreaker product by pipeline is the process objective, addition of a diluent such as gas condensate can be used to achieve a further reduction in viscosity. Recovery of the diluent after pipelining is an option.

The significance of the measured properties of residual fuel oil is dependent to a large extent on the ultimate uses of the fuel oil. Such uses include steam generation for various processes as well as electrical power generation and propulsion. Corrosion, ash deposition, atmospheric pollution, and product contamination are side effects of the use of residual fuel oil, and in particular cases properties such as vanadium, sodium, and sulfur contents may be significant.

Problems of handling and storage may also arise, particularly with higher-boiling fuel oil, because at ambient temperatures this type of fuel oil may be viscous and even approach a semisolid state. Although such fuel oil is usually stored in heated tanks, test methods to determine the low-temperature behavior of the fuel oil are necessary. In addition, because viscous or semisolid fuel oil should be preheated to obtain the correct injection (atomizing) conditions for efficient combustion, test methods that describe viscosity are also necessary.

10.3. TEST METHODS

Test methods of interest for hydrocarbon analysis of residual fuel oil include tests that measure physical properties such as elemental analysis, density, refractive index, molecular weight, and boiling range. There may also be some emphasis on methods that are used to measure chemical composition and structural analysis, but these methods may not be as definitive as they are for other petroleum products.

Testing residual fuel oil does not suffer from the issues that are associated with sample volatility, but the test methods are often sensitive to the presence of gas bubbles in the fuel oil. An air release test is available for application to lubricating oil (ASTM D-3427, IP 313) and may be applied, with modification, to residual fuel oil. However, with dark-colored samples, it may be difficult to determine whether all air bubbles have been eliminated. And, as with the analysis and testing of other petroleum products, the importance of correct sampling of fuel oil cannot be overemphasized, because no proper assessment of quality can be made unless the data are obtained on truly representative samples (ASTM D-270, IP 51).

10.3.1. Ash

The ash formed by the combustion of fuel oil (ASTM D-482, ASTM D-2415, IP 4) is, as defined for other products, the inorganic residue, free from carbonaceous matter, remaining after ignition in air of the residual fuel oil at fairly high temperatures. The ash content is not directly equated to mineral content but can be converted to mineral matter content by the use of appropriate formulae.

Residual fuel oil often contains varying amounts of ash-forming constituents (but seldom more than 0.2% w/w) such as organometallic complexes that are soluble, or inherent, in petroleum, from mineral matter from oil-bearing strata, or from contact of the crude oil with pipelines and storage tanks during transportation and subsequent handling. Additives used to improve particular fuel properties and carryover from refining processes

may also contribute to the ultimate amount of mineral matter in the fuel oil and may present an inflated measurement of the ash formed by combustion of the sample. Thus, although the total amounts of ash-forming constituents in different fuel oils may be similar, the compositions of the mineral constituents will depend on the crude oil origin as well as on the handling of the respective fuel oils. These constituents ultimately concentrate in the distillation residue, and so their presence will be reflected in the fuel oil ash.

The presence of sodium and vanadium complexes in the fuel oil ash can, under certain plant operating conditions, result in considerable harm to the equipment. Spalling and fluxing of refractory linings is associated with the presence of sodium in the fuel. Above a certain threshold temperature, which will vary from fuel to fuel, the oil ash will adhere to boiler superheater tubes and gas turbine blades, thus reducing the thermal efficiency of the plant. At higher temperatures, molten complexes of vanadium, sodium, and sulfur are produced that will corrode all currently available metals used in the construction of these parts of the plant. The presence of trace amounts (ASTM D-1318) of vanadium (ASTM D-1548, IP 285, IP 286) in fuel oil used in glass manufacture can affect the indicator of the finished product.

10.3.2. Asphaltene Content

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 exposure to thermal conditions (Speight, 1999; Speight, 2001, Speight and Ozum 2002).

In any of the methods for the determination of the asphaltene content (Speight et al., 1984), the residual fuel oil 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.

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 by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present

in a large excess, the yields of the asphaltene fraction will vary and will be erroneous (Speight, 1999).

Another method, not specifically described as an asphaltene separation method, is designed to remove pentane-insoluble constituents by membrane filtration (ASTM D-4055). In the method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer any particulates onto the filter, after which the filter (with particulates) is dried and weighed to give the pentane-insoluble constituents as a percentage by weight of the sample.

Particulates can also be determined by membrane filtration (ASTM D-2276, ASTM D-5452, ASTM D-6217, IP 415).

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 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 precipitating 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.

If the residual fuel oil is produced by a thermal process such as visbreaking, it may also be necessary to determine whether toluene-insoluble material is present by the methods, or modifications thereof, used to determine the toluene-insoluble material of tar and pitch (ASTM D-4072, ASTM D-4312). In these methods, a sample is digested at 95°C (203°F) for 25 min and then extracted with hot toluene in an alundum thimble. The extraction time is 18 h (ASTM D-4072) or 2 h (ASTM D-4312). The insoluble matter is dried and weighed.

10.3.3. Calorific (Heat of Combustion) Value

The calorific value (heat of combustion) of residual fuel oil (ASTM D-240, IP 12) is lower than that of lower-boiling fuel oil (and other liquid fuels) because of the lower atomic hydrogen-to-carbon ratio and the incidence of greater amounts of less combustible material, such as water and sediment, and generally higher levels of sulfur.

For most residual fuel oils, the range of calorific value is relatively narrow and limits are not usually included in the specifications. When precise determinations are not essential, values of sufficient accuracy may be derived

from calculations based on measurable physical properties (ASTM D-6446). In this test method, the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the hydrogen content (ASTM D-1018, ASTM D-1217, ASTM D-1298, ASTM D-3701, ASTM D-4052, ASTM D-4808, ASTM D-5291, IP 160, IP 365), density (ASTM D-129, ASTM D-1250, ASTM D-1266, ASTM D-2622, ASTM D-3120, IP 61, IP 107), and sulfur content (ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 336, IP 373) of the sample are determined by experimental test methods and the net heat of combustion is calculated with the values obtained by these test methods based on reported correlations.

10.3.4. Carbon Residue

The propensity of residual fuel oil for carbon formation and deposition under thermal conditions may be indicated by the one or more of three carbon residue tests.

Thus the specifications for the allowable amounts of carbon residue by the Conradson carbon residue test (ASTM D-189, IP 13), the Ramsbottom carbon residue test (ASTM D-524, IP 14), or the microcarbon carbon residue test (ASTM D-4530, IP 398) may be included in inspection data for fuel oil.

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 D-524, 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 cracks 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 D-4530, 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 D-4530, IP 398) are equivalent to those produced by the Conradson carbon 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.

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 data give an indication of the amount of coke that will be formed during exposure of the residual fuel oil to thermal effects. However, the significance of a carbon residue test relative to the combustion characteristics of the fuel is questionable because the significance of the test depends, to a large extent, on the particular process and handling conditions, specifically the introduction of residual fuel oil to heat in pipes as it passes to a furnace.

Other test methods that are used for determining the *coking value* of tar and pitch (ASTM D-2416, ASTM D-4715), which indicates the relative coke-forming properties of tars and pitches, might also be applied to residual fuel oil. Both test methods are applicable to tar and pitch with an ash content of ≤0.5% (ASTM D-2415). The former test method (ASTM D-2416) gives results close to those obtained by the Conradson carbon residue test (ASTM D-189 IP 13). However, in the latter test method (ASTM D-4715), a sample of tar (or pitch) is heated for a specified time at 550 ± 10°C (1022 ± 18°F) in an electric furnace. The percentage of residue is reported as the coking value. For residual fuel oil, the temperature of both test methods can be adjusted to the temperature that the fuel oil might experience in the pipe to the furnace, with a corresponding adjustment for the residence time in the pipe.

Finally, a method that is used to determine pitch volatility (ASTM D-4893) might also be used, on occasion, to determine the nonvolatility of residual fuel oil. In the method, an aluminum dish containing about 15 g of accurately weighed sample is introduced into the cavity of a metal block heated and maintained at 350°C (662°F). After 30 min, during which the volatiles are swept away from the surface of the sample by preheated nitrogen, the residual sample is taken out and allowed to cool down in the desiccator. Nonvolatility is determined by the sample weight remaining and reported as percentage w/w residue.

10.3.5. Composition

The composition of residual fuel oils is varied and is often reported in the form of four or five major fractions as deduced by adsorption chromatography (Fig. 10.1 and Fig. 10.2). In the case of cracked feedstocks, thermal decomposition products (carbenes and carboids) may also be present.

Column chromatography is used for several hydrocarbon type analyses that involve fractionation of viscous oils (ASTM D-2007, ASTM D-2549), including residual fuel oil. The former method (ASTM D-2007) advocates the use of adsorption on clay and clay-silica gel. followed by elution of the clay with pentane to separate saturates; elution of clay with acetone-toluene to separate polar compounds; and elution of the silica gel fraction with toluene to separate aromatic compounds. The latter method (ASTM D-2549) uses adsorption on a bauxite-silica gel column. Saturates are eluted with pentane; aromatics are eluted with ether, chloroform, and ethanol.

Several promising chromatographic techniques have been reported for the analysis of lubricant base oils. Rod thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), and supercritical fluid chromatography (SFC) have all been used for fuel oil analysis and base oil content.

In addition to carbon and hydrogen, high-molecular-weight fractions of crude oil often contain oxygen compounds, sulfur compounds, and nitrogen

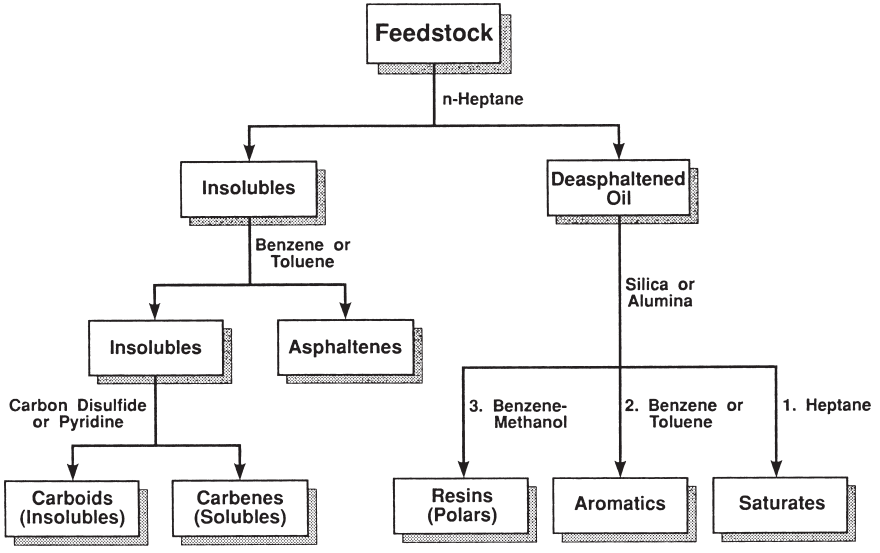

Figure 10.1. Separation of a feedstock into four major fractions

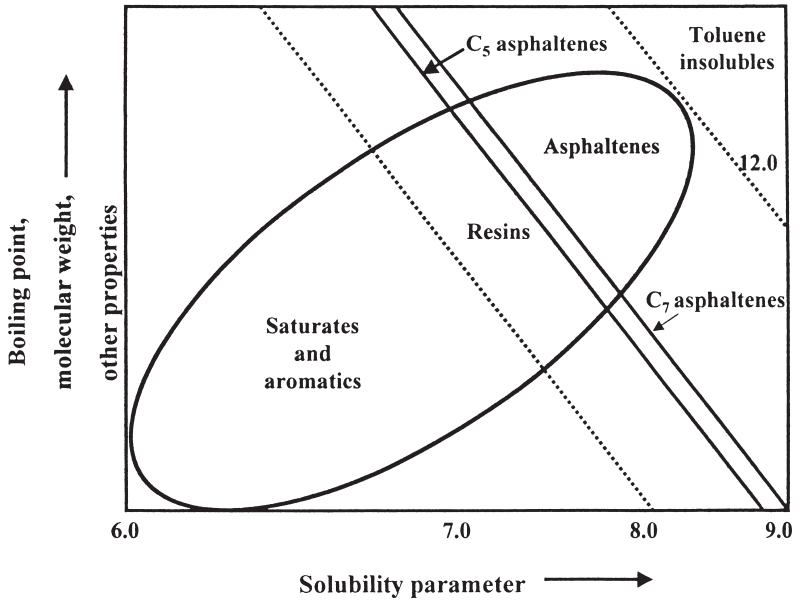

Figure 10.2. Representation of feedstock fractionation

compounds as well as trace amounts of metal-containing compounds. Determining the chemical form present for these elements provides additional important information. Finished products made with viscous oils may contain additives or contaminants that also require analysis. Thus *elemental analysis* also plays an important role in determining the composition of residual fuel oils.

Carbon and hydrogen are commonly determined by combustion analysis in which the sample is burned in an oxygen stream where carbon is converted to carbon dioxide and hydrogen to water. These compounds are absorbed, and the composition is determined automatically from mass increase (ASTM D-5291). Nitrogen may be determined simultaneously.

Sulfur is naturally present in many crude oils and petroleum fractions, most commonly as organic sulfides and heterocyclic compounds. Residual fuel oils are variable products whose sulfur contents depend not only on their crude oil sources but also on the extent of the refinery processing received by the fuel oil blending components. Sulfur, present in these fuel oils in varying amounts up to 4 or 5% w/w, is an undesirable constituent, and many refining steps aim to reduce the sulfur content to improve stability and reduce environmentally harmful emissions.

Hydrogen sulfide (H_2S) and mercaptans (R-SH) may be produced during thermal processes such as the visbreaking process and can occur in

fuel oil with other sulfur compounds that concentrate in the distillation residue. Without any further processing, such as hydrofining and caustic washing (Speight, 1999; Speight, 2000), these sulfur compounds remain in the fuel oil. The sulfur content of fuel oil obtained from petroleum residua and the atmospheric pollution arising from the use of these fuel oils is an important factor, and the increasing insistence on a low-sulfur-content fuel oil has increased the value of low-sulfur petroleum.

A considerable number of tests are available to estimate the sulfur in petroleum or to study its effect on various products, particularly hydrogen sulfide (ASTM D-5705, ASTM D-6021), that can result as a product of thermal processes, such as visbreaking. Hydrogen sulfide dissolved 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.

Of all the elements present in a normal residual fuel oil, vanadium, sodium, and sulfur contribute most to difficulties and problems that may arise in the industrial application of fuel oils. Sulfur contributes to the increasing problem of atmospheric pollution when sulfur oxides, produced on combustion of high-sulfur fuel oils, are emitted into the surrounding atmosphere of densely populated industrial areas or large towns. In specific applications fuel oil desulfurization may have to be used to comply with air pollution legislation.

The methods used to measure sulfur content vary depending on the sulfur concentration, viscosity or boiling range, and presence of interfering elements.

For the determination of sulfur contents of residual fuels a variety of procedures are available. The bomb (ASTM D-129, IP 61) and quartz tube (ASTM D-l55, IP 63) combustion methods have long been established. Other, more rapid techniques are becoming increasingly available, including high-temperature combustion (ASTM D-1552), X-ray absorption and fluorescence methods, and the Schoniger oxygen flask procedure.

The bomb method for sulfur determination (ASTM D-129) uses sample combustion in oxygen and conversion of the sulfur to barium sulfate, which is determined by mass. This method is suitable for samples containing 0.1–5.0% w/w sulfur and can be used for most low-volatility petroleum products. Elements that produce residues insoluble in hydrochloric acid

interfere with this method—this includes aluminum, calcium, iron, lead, and silicon plus minerals such as asbestos, mica, and silica—and an alternate method (ASTM D-1552) is preferred. This method describes three procedures: the sample is first pyrolyzed in either an induction furnace or a resistance furnace; the sulfur is then converted to sulfur dioxide; and the sulfur dioxide is either titrated with potassium iodate-starch reagent or analyzed by infrared spectroscopy. This method is generally suitable for samples containing from 0.06 to 8.0% w/w sulfur that distill at temperatures above 177°C (351°F).

Two methods describe the use of X ray techniques for sulfur determination and can be applied to the determination of sulfur in samples with sulfur content of 0.001–5.0% w/w (ASTM D-2622, ASTM D-4294). Oil viscosity is not a critical factor with these two methods, but interference may affect test results when chlorine, phosphorus, heavy metals, and possibly silicon are present. A method is also available for very low sulfur concentrations (ASTM D-4045). This is normally used for lower-viscosity fractions but may be used for some viscous oils that boil below 371°C (700°F). The method is designed to measure sulfur in the range of 0.02 to 10 ppm. Sulfur may also be determined along with metals (ASTM D-4927, ASTM D-4951, ASTM D-5185).

Nitrogen is present in residual fuel oils and is also a component of many additives used in petroleum products, including oxidation and corrosion inhibitors and dispersants. There are four ASTM standards describing analytical methods for nitrogen in viscous oils. The first (ASTM D-3228) is a standard wet chemical method and is useful for determining the nitrogen content of most viscous oils in the range from 0.03 to 0.10% w/w nitrogen. The other three methods are instrumental techniques; one involves nitrogen reduction, and the other two involve nitrogen oxidation. One method (ASTM D-3431) is an instrumental method where nitrogen is pyrolyzed under reducing conditions and converted to ammonia, which is measured coulometrically. This method is very useful in assessing feeds for catalytic hydrogenation processes, where nitrogen may act as a catalyst poison. Another method (ASTM D-4629) is useful for samples containing 0.3–100 ppm nitrogen and boiling higher than 400°C (752°F) but with viscosities of 10 cSt or less. In this method, organic nitrogen is converted to nitric oxide (NO) and then to excited nitrogen dioxide (NO_2) by reaction with oxygen and ozone. Energy emitted during decay of the excited nitrogen dioxide is measured with a photomultiplier tube. There is a method (ASTM D-5762) that is complementary to this one and is suitable for higher-viscosity viscous samples that contain from 40 to 10,000 ppm nitrogen.

The viscous fractions of crude oil often contain *metals* such as iron, nickel, and vanadium. Catalytic refining processes are often sensitive to metal contamination and, therefore, the type and quantity of metals must

be determined. In other cases such as lubricating oils, some metals are parts of compounds added to the petroleum component to enhance performance.

A standard wet chemical analysis (ASTM D-811) is available for determination of aluminum, barium, calcium, magnesium, potassium, silicon, sodium, tin, and zinc. The procedure involves a series of chemical separations with specific elemental analysis performed by using appropriate gravimetric or volumetric analyses.

The most commonly used methods for determining metal content in viscous oils are spectroscopic techniques. In one such method (ASTM D-4628), the sample is diluted in kerosene and burned in an acetylene-nitrous oxide flame of an M spectrophotometer. The method is suitable for oils in the lubricating oil viscosity range. It is designed to measure barium at concentrations of 0.005–1.0% w/w, calcium and magnesium at 0.002–0.3% w/w, and zinc at 0.002–0.2% w/w. Higher metal concentrations, such as are present in additives, can be determined by dilution. Lower concentrations in the range of 10–50 ppm can also be determined; however, the precision is poorer. An alternate test method (ASTM D-4927) is designed for unused lube oils containing metals at concentration levels of 0.03–1.0% w/w and sulfur at 0.01–2.0% w/w. Higher concentrations can be determined after dilution.

A third technique (ASTM D-4951) is used to determine barium, boron, calcium, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additive packages. Elements can generally be determined at concentrations of 0.01–1.0% w/w. The sample is diluted in mixed xylenes or other solvents containing an internal standard. The ICP method (ASTM D-708, ASTM D-5185) is also available. Sensitivity and useable range varies from one element to another, but the method is generally applicable from 1 to l00 ppm for contaminants and up to 1000–9000 ppm for additive elements:

Additive Elements	**Contaminant Elements**		
calcium	aluminum	lead	sodium
magnesium	barium	manganese	tin
phosphorus	boron	molybdenum	titanium
potassium	chromium	nickel	vanadium
sulfur	copper	silicon	
zinc	iron	silver	

Two procedures are described whereby either the sample is treated with acid to decompose the organic material and dissolve the metals or, alternatively, the sample is dissolved in an organic solvent. The first method is sensitive down to about 1 ppm; the precision statement is based on samples containing 1–10 ppm iron, 10–l00 ppm nickel, or 50–500 ppm vanadium

(ASTM D-5708). The second method provides an alternate method for analysis of crude oils and residuum (ASTM D-5863). The sensitivity range is 3.0–10 ppm for iron, 0.5–100 ppm for nickel, 0.1–20 ppm for sodium, and 0.5–500 ppm for vanadium. Higher concentrations may be determined after dilution.

A variety of *miscellaneous elements* can also occur in residual fuel oil fraction For example, *chlorine* is present as a chlorinated hydrocarbon and can be determined (ASTM D-808, ASTM D-1317, ASTM D-6160). A rapid test method suitable for analysis of samples by nontechnical personnel is also available (ASTM D-5384) that uses a commercial test kit where the oil sample is reacted with metallic sodium to convert organic halogens to halide, which is titrated with mercuric nitrate using diphenyl carbazone indicator. Iodides and bromides are reported as chloride.

Phosphorus is a common component of additives and appears most commonly as a zinc dialkyl dithiophosphate or a tri-aryl phosphate ester, but other forms also occur. Two wet chemical methods are available, one of which (ASTM D-1091) describes an oxidation procedure that converts phosphorus to aqueous orthophosphate anion. This is then determined by mass as magnesium pyrophosphate or photochemically as molybdivanadophosphoric acid. In an alternate test (ASTM D-4047), samples are oxidized to phosphate with zinc oxide, dissolved in acid, precipitated as quinoline phosphomolybdate, treated with excess standard alkali, and back-titrated with standard acid. Both of these methods are primarily used for referee samples. Phosphorus is most commonly determined with X-ray fluorescence (ASTM D-4927) or ICP (ASTM D-4951).

Correlative methods are derived relationships between fundamental chemical properties of a substance and measured physical or chemical properties. They provide information about an oil from readily measured properties (ASTM D-2140, ASTM D-2501, ASTM D-2502, ASTM D-3238).

One method (ASTM D-2501) describes the calculation of the viscosity-gravity coefficient (VGC)—a parameter derived from kinematic viscosity and density that has been found to relate to the saturate/aromatic composition. Correlations between the viscosity-gravity coefficient (or molecular weight and density) and refractive index to calculate carbon type composition in percentage of aromatic, naphthenic, and paraffinic carbon atoms are used to estimate of the number of aromatic and naphthenic rings present (ASTM D-2140, ASTM D-3238).

Another method (ASTM D-2502) permits estimation of molecular weight from kinematic viscosity measurements at 38 and 99°C (100 and 210°F) (ASTM D-445). It is applicable to samples with molecular weights in the range from 250 to 700 but should not be applied indiscriminately for oils that represent extremes of composition for which different constants are derived (Moschopedis et al., 1976).

However, data from correlative methods must not be confused with more fundamental measurements obtained by chromatography or mass spectroscopy. Correlative methods can be extremely useful when used to follow changes in a hydrocarbon mixture during processing. They are less reliable when comparing materials of different origin and can be very misleading when applied to typical or unusual compositions.

A major use for *gas chromatography* for hydrocarbon analysis has been simulated distillation, as discussed above. Other gas chromatographic methods have been developed for contaminant analysis (ASTM D-3524, ASTM D-4291)

The aromatic content of fuel oil is a key property that can affect a variety of other properties including viscosity, stability, and compatibility with other fuel oil or blending stock. Existing methods for this work use physical measurements and require suitable standards. Thus methods have been standardized with nuclear magnetic resonance (NMR) for hydrocarbon characterization (ASTM D-4808, ASTM D-5291, ASTM D-5292). The nuclear magnetic resonance method is simpler and more precise. Procedures are described that cover light distillates with a 15–260°C boiling range, middle distillates and gas oils with boiling ranges of 200–370°C and 370–510°C, and residuum boiling above 510°C. One of the methods (ASTM D-5292) is applicable to a wide range of hydrocarbon oils that are completely soluble in chloroform and carbon tetrachloride at ambient temperature. The data obtained by this method can be used to evaluate changes in aromatic contents of hydrocarbon oils resulting from process changes.

High ionizing voltage mass spectrometry (ASTM D-2786, ASTM D-3239) is also employed for compositional analysis of residual fuel oil. These methods require preliminary separation with elution chromatography (ASTM D-2549). A third method (ASTM D-2425) may be applicable to some residual fuel oil samples in the lower molecular weight range.

10.3.6. Density (Specific Gravity)

Density or specific gravity (relative density) is used whenever conversions must be made between mass (weight) and volume measurements. This property is often used in combination with other test results to predict oil quality, and several methods are available for measurement of density (or specific gravity). However, the density (specific gravity) (ASTM D-1298, IP 160) is probably of least importance in determining fuel oil performance but it is used in product control, in weight-volume relationships, and in the calculation of calorific value (heating value).

Two of the methods (ASTM D-287, ASTM D-1298) use an immersed hydrometer for measurement of density. The former method (ASTM

D-287) provides the results as API gravity. Two other methods (ASTM D-1480, ASTM D-1481) use a pycnometer to measure density or specific gravity and have the advantage of requiring a smaller sample size and can be used at higher temperatures than is normal providing that the vapor pressure of the liquid does not exceed specific limits at the temperature of the test. Two other test methods (ASTM D-4052, ASTM D-5002) measure density with a digital density analyzer. This device determines density by analysis of the change in oscillating frequency of a sample tube when filled with the test sample.

Another test method (ASTM D-4052) covers the determination of the density or specific gravity of viscous oils, such as residual fuel oil, that are liquid at test temperatures between 15 and 35°C (59 and 95°F). However, application of the method is restricted to liquids with vapor pressures below 600 mmHg and viscosity below 15,000 cSt at the temperature of test. In addition, and this is crucial for residual fuel oil, this test 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.

10.3.7. Elemental Analysis

Elemental analysis of fuel oil often plays a more major role that it may appear to do in the lower-boiling products. Aromaticity (through the atomic hydrogen-to-carbon ratio), sulfur content, nitrogen content, oxygen content, and metals content are all important features that can influence use of residual fuel oil.

Carbon content and *hydrogen content* can be determined simultaneously by the method designated for coal and coke (ASTM D-3178) or by the method designated for municipal solid waste (ASTM E-777). However, as with any analytical method, the method chosen for the analysis may be subject to the peculiarities or character of the feedstock under investigation and should be assessed in terms of accuracy and reproducibility. The methods that are designated for elemental analysis are:

1. *Carbon* and *hydrogen content* (ASTM D-1018, ASTM D-3178, ASTM D-3343, ASTM D-3701, ASTM D-5291, ASTM E-777, IP 338);
2. *Nitrogen content* (ASTM D-3179, ASTM D-3228, ASTM D-3431, ASTM E-148, ASTM E-258, ASTM D-5291, and ASTM E-778);
3. *Oxygen content* (ASTM E-385), and
4. *Sulfur content* (ASTM D-124, ASTM D-129, ASTM D-139, ASTM D-1266, ASTM D-1552, ASTM D-1757, ASTM D-2622, ASTM D-2785, ASTM D-3120, ASTM D-3177, ASTM D-4045 and ASTM D-4294, ASTM E-443, IP 30, IP 61, IP 103, IP 104, IP 107, IP 154, IP 243).

The hydrogen content of fuel oil can also be measured by low-resolution magnetic resonance spectroscopy (ASTM D-3701, ASTM D-4808). The method is claimed to provide a simple and more precise alternative to existing test methods, specifically combustion techniques (ASTM D-5291), for determining the hydrogen content of a variety of petroleum-related materials.

Nitrogen occurs in residua and, therefore, in residual fuel oil and causes serious environmental problems as a result, especially when the levels exceed 0.5% by weight, as happens often in residua. In addition to the chemical character of the nitrogen, the amount of nitrogen in a feedstock determines the severity of the process, the hydrogen requirements, and to some extent, the sediment formation and deposition.

The determination of nitrogen in petroleum products is performed regularly by the Kjeldahl method (ASTM D-3228), the Dumas method, and the microcoulometric (ASTM D-3431) method. The chemiluminescence method is the most recent technique applied to nitrogen analysis for petroleum and is used to determine the amount of chemically bound nitrogen in liquid samples.

In the method, the samples are introduced to the oxygen-rich atmosphere of a pyrolysis tube maintained at 975°C (1785°F). Nitrogen in the sample is converted to nitric oxide during combustion, and the combustion products are dried by passage through magnesium perchlorate [$Mg(ClO_4)_2$] before entering the reaction chamber of a chemiluminescence detector. In the detector, ozone reacts with the nitric oxide to form excited nitrogen dioxide:

$$NO + O_3 = NO_2^* + O_2$$

Photoemission occurs as the excited nitrogen dioxide reverts to the ground state:

$$NO_2^* = NO_2 + h\nu$$

The emitted light is monitored by a photomultiplier tube to yield a measure of the nitrogen content of the sample. Quantitation is based on comparison with the response for carbazole in toluene standards.

Oxygen is one of the five (C, H, N, O, and S) major elements in fuel oil but rarely exceeds 1.5% by weight, unless oxidation has occurred during transportation and storage. Many petroleum products do not specify a particular oxygen content, but if the oxygen compounds are present as acidic compounds such as phenols (Ar-OH) and naphthenic acids (cycloalkyl-COOH), they are controlled in different specifications by a variety of tests. The *total acidity* (ASTM D-974, IP 139, IP 273) is determined for many products, especially fuels and fuel oil. Oxygen-containing impurities in the

form of *gum* are determined by the *existent gum* (ASTM D-381, IP 131) and *potential gum* (ASTM D-873, IP 138) test methods. Elemental analysis of the gum can then provide its composition, with some indication of the elements (other than carbon and hydrogen) that played a predominant role in its formation.

Being the third most common element (after carbon and hydrogen) in petroleum product, *sulfur* has been analyzed extensively. Analytical methods range from elemental analyses to functional group (sulfur type) analyses to structural characterization to molecular speciation (Speight, 2001). Of the methods specified for the determination of sulfur (Speight, 2001), the method applied to the corrosion effect of sulfur in extremely important for liquid fuels. In this method (ASTM D-1266, IP 154), fuel corrosivity is assessed by the action of the fuel on a copper strip (*the copper strip test*), which helps determine any discoloration of the copper due to the presence of corrosive compounds. The copper strip is immersed in the fuel and heated at 100°C (212°F) for 2 h in a bomb. A test using silver as the test metal (IP 227) has also been published. Mercaptans are usually the corrosive sulfur compounds of reference, and metal discoloration is due to formation of the metal sulfide. Thus mercaptan sulfur is an important property of potential fuels. In addition to the copper strip test, the mercaptan sulfur (R-SH) content (ASTM D-1219, IP 104) provides valuable information. As an alternative to determining the mercaptan content, a negative result in the *Doctor test* (ASTM D-484, IP 30) may also be acceptable for the qualitative absence of mercaptans. The copper strip method (ASTM D-130, ASTM D-849, ASTM D-4048, IP 154) may also be used to determine the presence of corrosive sulfur compounds in residual fuel oil.

The determination of sulfur in liquid products by X-ray fluorescence (ASTM D-2622, IP 336) has become an extremely well used method over the past two decades. This method can be used to determine the amount of sulfur in homogeneous liquid petroleum hydrocarbons over the range of 0.1–6.0% by weight. Samples with a sulfur content above this range may be determined after dilution in toluene. The method utilizes the principle that when a sample is irradiated with a Fe^{55} source, fluorescent X rays result. The sulfur Kα fluorescence and a background correction at adjacent wavelengths are counted. A calibration of the instrument, wherein the integration time for counting is adjusted such that the displayed signal for the background-corrected radiation equals the concentration of the calibration standard, gives a direct readout of the weight percent sulfur in the sample. Interfering elements include aluminum, silicon, phosphorus, chlorine, argon, and potassium. Generally the amounts of these elements are insufficient to affect sulfur X ray counts in samples covered by this method. Atmospheric argon is eliminated by a helium purge.

It is also possible to determine nitrogen and sulfur simultaneously by chemiluminescence and fluorescence. An aliquot of the sample undergoes high-temperature oxidation in a combustion tube maintained at 1050°C (1920°F). Oxidation of the sample converts the chemically bound nitrogen to nitric oxide (NO) and sulfur to sulfur dioxide (SO_2). In the nitrogen detector, ozone reacts with the nitric oxide to form excited nitrogen dioxide (NO_2). As the nitrogen dioxide reverts to its ground state, chemiluminescence occurs, and this light emission is monitored by a photomultiplier tube. The light emitted is proportional to the amount of nitrogen in the sample. In the sulfur detector, the sulfur dioxide is exposed to ultraviolet radiation and produces a fluorescent emission. This light emission is proportional to the amount of sulfur and is also measured by a photomultiplier tube. Quantitation is determined by a comparison to the responses given by standards containing carbazole and dimethyl sulfoxide in xylene.

Oxidative microcoulometry has become a widely accepted technique for the determination of low concentrations of sulfur in petroleum and petroleum products (ASTM D-3120). The method involves combustion of the sample in an oxygen-rich atmosphere followed by microcoulometric generation of tri-iodide ion to consume the resultant sulfur dioxide. This distinguishes the technique from reductive microcoulometry, which converts sulfur in the sample to hydrogen sulfide that is titrated with coulometrically generated silver ion.

Although sodium azide is included in the electrolyte of the microcoulometric titration to minimize halogen and nitrogen interferences, the method is not applicable when chlorine is present in excess of 10 times the sulfur level or the nitrogen content exceeds 10% by weight. Heavy metals in excess of 500 mg/kg also interfere with this method.

10.3.8. Flash Point

As for all petroleum products, considerations of safety in storage and transportation and, more particularly, contamination by more volatile products are required. This is usually accommodated by the Pensky–Martens flash point test (ASTM D-93, IP 34). For the fuel oil, a minimum flash point of 55°C (131°F) or 66°C (150°F) is included in most specifications.

10.3.9. Metals Content

Heteroatoms (*nitrogen*, *oxygen*, *sulfur*, and *metals*) are found in every crude oil, and the concentrations must be reduced to convert the oil to transportation fuel. The reason is that if nitrogen and sulfur are present in the final fuel during combustion, nitrogen oxides (NO_x) and sulfur oxides (SO_x) form, respectively. In addition, metals affect the use of

residual fuel oil through adverse effects such as by causing corrosion or by deposition.

The nature of the process by which residual fuel oil is produced virtually dictates that all the metals in the original crude oil can occur in the residuum (Speight, 2001) and, thus, in the residual fuel. Metallic constituents that may actually *volatilize* under the distillation conditions and appear in the higher-boiling distillates are the exceptions and can appear in distillate fuel oil.

The analysis for metal constituents in residua can be accomplished by several instrumental techniques: inductively coupled argon plasma (ICAP) spectrometry, atomic absorption (AA) spectrometry, and X-ray fluorescence (XRF) spectrometry. Each technique has limitations in terms of sample preparation, sensitivity, sampling, time for analysis, and overall ease of use. Thus a number of tests (ASTM D-482, D-1026, D-1262, D-1318, D-1368, D-1548, D-1549, D-2547 D-2599, D-2788, D-3340, D-3341, and D-3605) have been designated to determine metals in petroleum products, either directly or as the constituents of combustion ash, based on a variety of techniques. At the time of this writing, the specific test for the determination of metals in whole feeds has not been designated. However, this task can be accomplished by combustion of the sample so that only inorganic ash remains (ASTM D-482). The ash can then be digested with an acid and the solution can be examined for metal species by atomic absorption (AA) spectroscopy (IP 288, IP 285) or by inductively coupled argon plasma spectrometry (ASTM C-1109, ASTM C-1111).

Atomic absorption provides very high sensitivity but requires careful subsampling, extensive sample preparation, and detailed sample-matrix corrections. X-ray fluorescence requires little in terms of sample preparation but suffers from low sensitivity and the application of major matrix corrections. Inductively coupled argon plasma spectrometry provides high sensitivity and few matrix corrections but requires a considerable amount of sample preparation depending on the process stream to be analyzed.

In the inductively coupled argon plasma emission spectrometer method, nickel, iron, and vanadium content of gas oil samples in the range from 0.1 to 100 mg/kg. Thus a 10-g sample of gas oil is charred with sulfuric acid and subsequently combusted to leave the ash residue. The resulting sulfates are then converted to their corresponding chloride salts to ensure complete solubility. A barium internal standard is added to the sample before analysis. In addition, the use of the ICAP method for the analysis of nickel, vanadium, and iron present counteracts the two basic issues arising from metals analysis. The most serious issue is the fact that these metals are partly or totally in the form of volatile, chemically stable porphyrin complexes and extreme conditions are needed to destroy the complexes without losing the metal through volatilization of the complex. The

second issue is that the alternate direct aspiration of the sample introduces large quantities of carbon into the plasma. This carbon causes marked and somewhat variable background changes in all direct measurement techniques.

Finally, the analytical method should be selected depending on the sensitivity required, the compatibility of the sample matrix with the specific analysis technique, and the availability of facilities. Sample preparation, if it is required, can present problems. Significant losses can occur, especially in the case of organometallic complexes, and contamination of environmental sample is of serious concern. The precision of the analysis depends on the metal itself, the method used, and the standard used for calibration of the instrument.

10.3.10. Molecular Weight

Molecular weight is a physical property that can be used in conjunction with other physical properties to characterize residual fuel oil. Because residual fuel oil is a mixture having a broad boiling range, measurement of molecular weight provides the mass-average molecular weight or the number-average molecular weight.

Molecular weight may be calculated from viscosity data (ASTM D-2502) by using centistoke viscosity at 38°C (100°F) and 99°C (210°F). The method is generally applicable to sample having a molecular weight in the range of 250 to 700. Samples with unusual composition, such as aromatic-free white mineral oils, or oils with very narrow boiling range, may give atypical results.

For samples with higher molecular weight (up to 3000 or more) and unusual composition or for polymers, another method (ASTM D-2503) is recommended. This method uses a vapor pressure osmometer to determine molecular weight. Low-boiling samples may not be suitable if their vapor pressure interferes with the method.

Another method (ASTM D-2878) provides a procedure to calculate these properties from test data on evaporation. In the method, the sample is dissolved in an appropriate solvent. A drop each of this solution and the solvent are suspended on separate thermistors in a closed chamber saturated with solvent vapor. The solvent condenses on the sample drop and causes a temperature difference between the two drops. The resultant change in temperature is measured and used to determine the molecular weight of the sample by reference to a previously prepared calibration curve. This procedure is based on an older method (ASTM D-972) in which the sample can be partly evaporated at a temperature of 250–500°C (482–932°F), and fluids not stable in this temperature range may require special treatment.

10.3.11. Pour Point

The *pour point* (ASTM D-97, ASTM D-5949, ASTM D-5950, ASTM D-5853, ASTM D-5985, IP 15) is the lowest temperature at which oil will flow under prescribed conditions. The test method for determining the solidification point (ASTM D-1493) might also be applied to residual fuel oil.

One of the main attributes of liquid fuels is the relative ease with which they can be transferred from one place to another, but it is still necessary to have some indication of the lowest temperature at which this may be achieved. Depending on the storage conditions and the application of the fuel, limits are placed on the pour point. Storage of the higher-viscosity fuel oils in heated tankage will permit of higher pour points than would otherwise be possible. Although the failure to flow can generally be attributed to the separation of wax from the fuel, it can also, in the case of very viscous fuels, be due to the effect of viscosity.

The pour point of residual fuel oil may be influenced by the previous thermal history of the residual fuel oil and the fact that any loosely knit wax structure built up on cooling the fuel can, generally, be readily broken up by the application of a little pressure, thus allowing fuels to be pumped at temperatures below their pour point temperatures. The usefulness of the pour point test in relation to residual fuel oils is, therefore, open to question, and the tendency to regard it as the limiting temperature at which a fuel will flow can be misleading unless it is correlated with low-temperature viscosity.

The pour point test is still included in many specifications but not in some (ASTM D-396, BS 2869) for assessing the pumpability characteristics of residual fuel oil (ASTM D-3245). Pour point procedures involving various preheat treatments before the pour point determination and the use of viscosity at low temperatures have been proposed. The fluidity test (ASTM D-l659) is one such procedure as is the pumping temperature test (ASTM D-3829); another test, based on viscosity measurements (IP 230), is also available.

10.3.12. Refractive Index

The *refractive index* is the ratio of the velocity of light in air to the velocity of light in the measured substance. The value of the refractive index varies inversely with the wavelength of light used and the temperature at which the measurements are taken. The refractive index is a fundamental physical property that can be used for the determination of the gross composition of residual fuel oil and often requires its measurement at elevated temperature. In addition, the refractive index of a substance is related to its chemical composition and may be used to draw conclusions about molecular structure.

Two methods (ASTM D-1218, ASTM D-1747) are available for measuring the refractive index of viscous liquids. Both methods are limited to lighter-colored samples for best accuracy. The latter test method (ASTM D-1747) covers the measurement of refractive indexes of light-colored residual fuel oil at temperatures from 80 to 100°C (176–212°F). Temperatures lower than 80°C (176°F) may be used provided that the melting point of the sample is at least 10°C (18°F) below the test temperature. This test method is not applicable, within reasonable standards of accuracy, to liquids having darker residual fuel oil (having a color darker than ASTM Color No. 4; ASTM D-1500).

10.3.13. Stability

The problem of instability in residual fuel oil may manifest itself either as waxy sludge deposited at the bottom of an unheated storage tank or as fouling of preheaters on heating of the fuel to elevated temperatures.

Problems of thermal stability and incompatibility in residual fuel oils are associated with those fuels used in oil-fired marine vessels, where the fuel is usually passed through a preheater before being fed to the burner system. In earlier days this preheating, with some fuels, could result in the deposition of asphaltic matter culminating, in the extreme case, in blockage of preheaters and pipelines and even complete combustion failure.

Asphaltene-type deposition may, however, result from the mixing of fuels of different origin and treatment, each of which may be perfectly satisfactory when used alone. For example, straight-run fuel oils from the same crude oil are normally stable and mutually compatible whereas fuel oils produced from thermal cracking and visbreaking operations that may be stable can be unstable or incompatible if blended with straight-run fuels and vice versa (ASTM D-1661).

Another procedure for predicting the stability of residual fuel oil involves the use of a spot test to show compatibility or cleanliness of the blended fuel oil (ASTM D-2781, ASTM D-4740). The former method (ASTM D-2781) covers two spot test procedures for rating a residual fuel with respect to its compatibility with a specific distillate fuel. Procedure A indicates the degree of asphaltene deposition that may be expected in blending the components and is used when wax deposition is not considered a fuel application problem. Procedure B indicates the degree of wax and asphalt deposition in the mixture at room temperature. The latter method (ASTM D-4740) is applicable to fuel oils with viscosities up to 50 cSt at 100°C (212°F) to identify fuels or blends that could result in excessive centrifuge loading, strainer plugging, tank sludge formation, or similar operating problems. In the method, a drop of the preheated sample is put on a test paper and placed in an oven at 100°C. After 1 h, the test paper is

removed from the oven and the resultant spot is examined for evidence of suspended solids and rated for cleanliness with the procedure described in the method. In a parallel procedure for determining *compatibility*, a blend composed of equal volumes of the fuel oil sample and the blend stock is tested and rated in the same way as just described for the *cleanliness* procedure.

For oxidative stability and the tendency to corrode metals, as may occur in pipes and burners, a test method (ASTM D-4636) is available to determine resistance to oxidation and corrosion degradation and their tendency to corrode various metals. The test method consists of one standard and two alternative procedures. A particular specification must establish which of these tests should be used. A large glass tube containing an oil sample and metal specimens is placed in a constant-temperature bath (usually from 100–360°C) and heated for the specified number of hours while air is passed through the oil to provide agitation and a source of oxygen. Corrosiveness of the oil is determined by the loss in metal mass and microscopic examination of the sample metal surface(s). Oil samples are withdrawn from the test oil and checked for changes in viscosity and acid number as a result of the oxidation reactions. At the end of the test the amount of the sludge present in the oil remaining in the same tube is determined by centrifugation. Also, the quantity of oil lost during the test is determined gravimetrically. Metals used in the basic test and alternative test are aluminum, bronze, cadmium, copper, magnesium, silver, steel, and titanium. Other metals may also be specified as determined by the history and storage of the fuel oil.

10.3.14. Viscosity

Viscosity is an important property of residual fuel oils because it provides information on the ease (or otherwise) with which a fuel can be transferred, under the prevailing temperature and pressure conditions, from storage tank to burner system. Viscosity data also indicate the degree to which a fuel oil must be preheated to obtain the correct atomizing temperature for efficient combustion. Most residual fuel oils function best when the burner input viscosity lies within a certain specified range.

The Saybolt Universal and Saybolt Furol viscometers are widely used in the U.S. and the Engler viscometer in Europe. In the U.S., viscosities of the lighter fuel grades are determined with the Saybolt Universal instrument at 38°C (100°F); for the heaviest fuels the Saybolt Furol viscometer is used at 50°C (122°F). Similarly, in Europe, the Engler viscometer is used at temperatures of 20°C (68°F), 50°C (122°F), and in some instances 100°C (212°F). The use of these empirical procedures for fuel oils is being superseded by the kinematic system (ASTM D-396, BS 2869) specifications for fuel oils.

The determination of residual fuel oil viscosities is complicated by the fact that some fuel oils containing significant quantities of wax do not behave as simple Newtonian liquids in which the rate of shear is directly proportional to the shearing stress applied. At temperatures in the region of 38°C (100°F) these fuels tend to deposit wax from solution, with a resulting adverse effect on the accuracy of the viscosity result unless the test temperature is raised sufficiently high for all wax to remain in solution. Although the present reference test temperature of 50°C (122°F) is adequate for use with the majority of residual fuel oils, there is a growing trend of opinion in favor of a higher temperature (82°C/180°F) particularly in view of the availability of waxier fuel oils.

Anomalous viscosity in residual fuel oils is best shown by plotting the kinematic viscosity determined at the normal test temperature and at two or three higher temperatures on viscosity-temperature charts (ASTM D-341). These charts are constructed so that, for a Newtonian fuel oil, the temperature-viscosity relationship is linear. Nonlinearity at the lower end of the applicable temperature range is normally considered evidence of non-Newtonian behavior. The charts are also useful for the estimation of the viscosity of a fuel oil blend from knowledge of the component viscosities and for calculation of the preheat temperature necessary to obtain the required viscosity for efficient atomization of the fuel oil in the burner.

Although it is considered a technical advantage to specify kinematic viscosity, the conventional viscometers are still in wide use and it may be convenient, or even necessary, to be able to convert viscosities from one system to another. Provision is made (ASTM D-2161) for the conversion of kinematic viscosity to Saybolt Universal and Furol viscosity and (in IP standards) for conversion to Redwood viscosity:

Kinematic viscosity at 50°C (122°F)	cSt	36	125	370	690
Kinematic viscosity at 38°C (100°F)	cSt	61	—	—	—
Redwood No. 1 viscosity at 50°C (122°F)	s	148	510	1500	2800
Redwood No. 1 viscosity at 38°C (100°F)	s	250	1000	3500	7000
Saybolt Universal viscosity at 38°C (100°F)	s	285	1150	4000	8000
Saybolt Furol viscosity at 50°C (122°F)	s	—	60	175	325
Engler degrees at 50°C (122°F)		4.8	16.5	48.7	91.0

10.3.15. Volatility

Four distillation methods are in common use for determining the boiling range and for collecting fractions from residual fuel oil. Such methods are rarely used for characterization of the fuel oil but do warrant mention here because of their application to fuel oil when desired.

One method (ASTM D-1160) is probably the best known and most widely used of the methods for distillation of higher-boiling petroleum products and uses vacuum distillation. The method is applicable to samples that can be at least partially volatilized at temperature up to 400°C (752°F) and pressure in the range of 1–50 mmHg. The distillation temperature at vacuum is converted to atmospheric equivalent temperatures.

Another method (ASTM D-447) is designed for characterization of these narrow boiling fractions. Another method (ASTM D-2892) applies to a wide range of products and uses a column with 15 theoretical plates and a 5:1 reflux ratio. The distillation is started at atmospheric pressure until the vapor temperature reaches 210°C (410°F). Distillation is continued at vacuum (l00 mmHg) until the vapor temperature again reaches 210°C (410°F) or cracking is observed.

With very heavy crude oil or viscous products, a preferred alternate distillation method (ASTM D-5236) should be used (instead of ASTM D-2892) for heavy crude oil above a 400°C (752°F) cut point. In the *spinning band* method (Fig. 10.3), fractions of feedstocks such as residual fuel oil with an initial boiling point above room temperature at atmospheric pressure can be investigated. For such materials, the initial boiling point of the sample should exceed room temperature at atmospheric pressure. The distillation is terminated at an atmospheric equivalent temperature of 524°C (975°F) and a pot temperature of 360°C (680°F).

In the method, samples are distilled under atmospheric and reduced pressures in a still equipped with a spinning band column. Vapor temperatures are converted to atmospheric equivalent temperatures and can be plotted as a function of volume or weight percent distilled to yield a distillation profile. The spinning band, which effectively provides a large contact area between the liquid phase and the vapor phase, increases the number of theoretical plates in the column and thus its fractionating efficiency. Readings of vapor temperature (which is convertible to atmospheric equivalent temperature) and distillate volume (which is convertible to percent by volume) are used to plot a distillation curve. Distillate yields for naphtha, light gas oil, heavy gas oil, and residue fractions are determined on a gravimetric basis.

Another method, *short path distillation*, produces a single distillate and a single residue fraction defined by the operating temperature and pressure of the still. This procedure is used to generate high-boiling-point fractions with end points up to 700°C (1290°F) for further analysis. Because only one cut temperature is used in each run, generation of a distillation curve with this equipment would be time consuming. In the method, the material to be fractionated is introduced at a constant rate onto the hot inner wall of the evaporator under high vacuum. Rotating (Teflon) rollers ensure that the film on the wall is kept thin. The feedstock is progressively

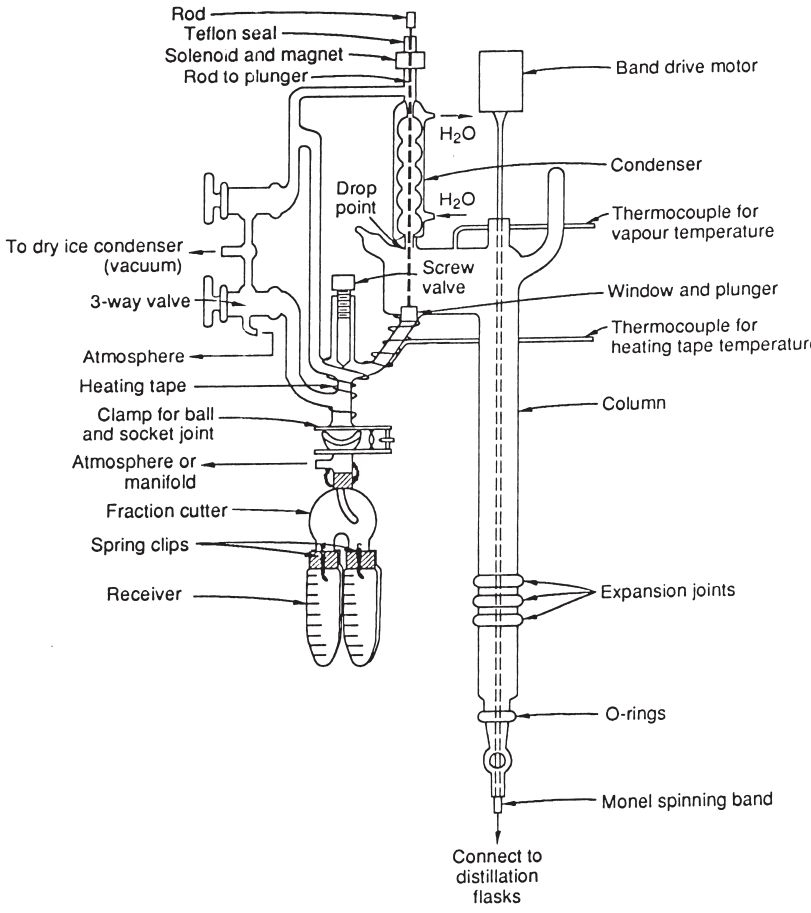

Figure 10.3. The spinning band equipment

distilled at the fixed conditions of temperature and pressure. The distillate vapors condense on a concentric cold surface (60°C/140°F) placed a short distance from the hot wall inside the still. The condensate then drains by gravity to the base of the *cold finger*, where it is collected. The residue drains down the hot wall and is collected through a separate port.

However, unless a distillation method is required by specification or the collected fractions are needed for further testing, gas chromatographic methods are now preferred for determining the boiling range of petroleum fractions, and detailed information for samples with a final boiling point no higher than 538°C (1000°F) at atmospheric pressure and a boiling range greater than 55°C (100°F) is available (ASTM D-2887).

10.3.16. Water

Contamination in residual fuel oil may be indicated by the presence of excessive amounts of water, emulsions, and inorganic material such as sand and rust. Appreciable amounts of sediment in a residual fuel oil can foul the handling facilities and give problems in burner mechanisms. Blockage of fuel filters (ASTM D-2068, ASTM D-6426) due to the presence of fuel degradation products may also result. This aspect of fuel quality control may be dealt with by placing restrictions on the water (ASTM D-95, IP 74), sediment by extraction (ASTM D-473, IP 53), or water and sediment (ASTM D-96, IP 75) values obtained for the fuel.

In any form, water and sediment are highly undesirable in fuel oil ,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 determination of quality.

The Karl Fischer test method (ASTM D-1364, ASTM D-6304) covers the direct determination of water in petroleum products. In the test, the sample injection in the titration vessel can be performed on a volumetric or gravimetric basis. Viscous samples, such as residual fuel oil, 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 can be determined simultaneously (ASTM D-96, ASTM D-1796, ASTM D-4007, IP 75, IP 359) by the centrifuge method. Known volumes of residual fuel oil 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. In the unlikely event that the residual fuel oil 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), a 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.

In a test specifically designed for residual fuel oil (ASTM D-4870, IP 375), a 10-g sample of oil is filtered through the prescribed apparatus at 100°C. After washing with the solvent and drying, the total sediment on the filter medium is weighed. The test is to be carried out in duplicate.

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CHAPTER

11

MINERAL OIL (WHITE OIL)

11.1. INTRODUCTION

In the present context, the term *mineral oil* or *white oil* refers to colorless or very pale oils within the lubricating oil class as regards carbon number and boiling range (Table 11.1, Fig. 11.1). Minerals (mineral) oils belong to two main groups, medicinal (pharmaceutical) oils and technical oils, the chief difference being degree of refining (Gruse and Stevens, 1960; Guthrie, 1967; Biske, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Warne, 1998; Speight, 2000; Banaszewski and Blythe, 2000).

Medicinal oils represent the most refined of the bulk petroleum products, especially when the principal use is for the pharmaceutical industry. Thus mineral oil destined for pharmaceutical purposes must meet stringent specifications to ensure that the oil is inert and that it does not contain any materials that are suspected to be toxic. Technical mineral oil (as opposed to pharmaceutical mineral oil) must meet much less stringent specifications requirements because the use is generally for transformer oil, cosmetic preparations (such as hair cream), in the plastics industry, and in textiles processing. Many of the same test methods are applied to all mineral oils, although the specifications will differ and oils for different uses will have to meet different standards of purity.

Technical oils find uses in different industries but in particular the electrical industry, where there is frequent use of transformer oil. Transformer oil can be divided into two main groups: (a) oils for transformers and switch gear and (b) oils for power cables; this latter group can be further subdivided into thin oils, for use in oil-filled (*hollow core*) cables, and more viscous oils, sometimes used as such in cable insulation but more commonly as components of cable impregnation compounds.

11.2. PRODUCTION AND PROPERTIES

Mineral oils are produced from selected petroleum fractions that are distilled to provide finished products with the desired viscosity. In addition to

Table 11.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

viscosity, properties considered during feedstock selection include pour point, cloud point, distillation range, smoke point, specific gravity, among others.

Typically, mineral oil is distilled to specification from the required crude oil fraction followed by pretreatment by solvent extraction, hydrotreating, and dewaxing (Gruse and Stevens, 1967; Speight, 2000 and references cited therein). Application of hydrotreating (Speight, 2000) means that mineral oil can be produced without acid treatment. However, on occasion, there is still the need to exhaustively treat the selected feedstock with concentrated sulfuric acid (gaseous sulfur trioxide treatment also may be used) to remove the aromatic, unsaturated hydrocarbons and other impurities. Petroleum sulfonic acids, produced as by-products during acid treatment, are removed by extraction and neutralization. The oil can be refined even further to an ultimate degree of purity by adsorption.

The fraction chosen for refining may have been subjected to a preliminary refining with a differential solvent. The exact procedure for the acid treatment varies (Speight, 2000), but a preliminary acid treatment (chiefly for drying) may be followed by incremental addition of as much as 50% by volume of acid as strong as 20% fuming sulfuric acid. The sludge is promptly removed to limit oxidation-reduction reactions; the time, temperature, and method of application depend on the type of charge stock and the desired degree of refining. The product is neutralized with alkali and washed with ethyl or isopropyl alcohol or acetone to remove the oil-soluble sulfonic *mahogany acids*; water-soluble *green*

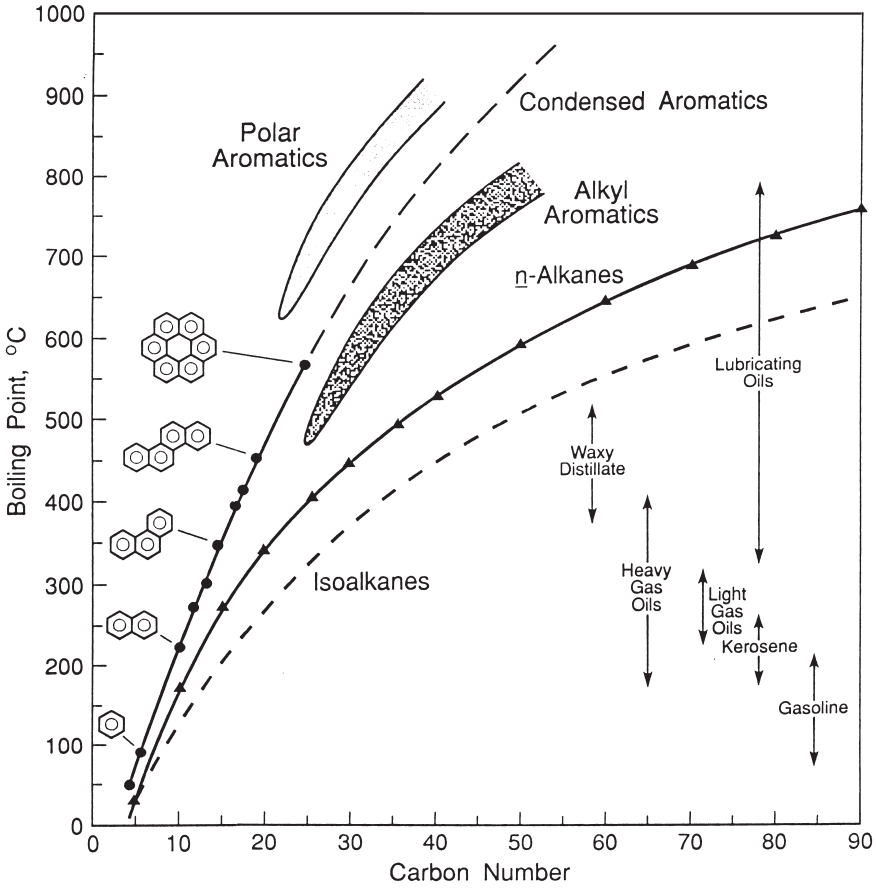

Figure 11.1. Boiling point and carbon number for various hydrocarbons and petroleum products

acids are recovered from the alkali washings. The treated oil is further refined and decolorized by adsorption, either by percolation or by contact with clay.

11.3. TEST METHODS

Many test methods are available to determine whether the quality prescribed by consumers for mineral oils is present. In all cases, tests that are carried out for lower-molecular-weight products and for higher-molecular-weight products are of lesser consequence with mineral oil. The stringent methods of refining (purification) remove many of the impurities, of which

ash-forming constituents can be cited as one example, making the test for such constituents redundant. If, for some reason, ash-forming constituents are believed to be present in the mineral oil, the test methods for ash (the presence of ash-forming constituents) that are applied to distillate fuel oil and top residual fuel oil can be applied to mineral oil.

But first, although the importance of careful sampling of any product that is to undergo testing is self-evident, very special precautions must be taken in the case of insulating oils (ASTM D-923, IP 51), for which special techniques are recommended. Precautions that are stipulated are mainly concerned with the avoidance of contamination that would affect electrical tests.

The main requirement of a *transformer oil* is that it should act as a heat transfer medium to ensure that the operating temperature of a transformer does not exceed acceptable limits. However, the deterioration of transformer oils in service is closely connected with oxidation by air, which brings on deposition of sludge and the development of acids, resulting in overheating and corrosion, respectively (ASTM D-4310). The sludge formed is usually attributed to the direct oxidation of the hydrocarbon constituents to oil-insoluble products.

Mineral oils used as *insecticides* require measurement of molecular weight (ASTM D-2502, ASTM D-2503, ASTM D-2878) and composition because the structure of the constituents appears to be a factor in determining the insecticide power of these oils. Olefins and aromatics are both highly toxic to insects, but they also have a detrimental effect on plants; thus spray oils generally receive some degree of refining, especially those of the summer oil type that come into contact with foliage.

11.3.1. Acidity or Alkalinity

The *acid number*—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 with *p*-naphtholbenzein indicator solution (ASTM D-974, IP 139). However, many higher-molecular-weight oil products (dark-colored oils), which cannot be analyzed for acidity because of obscurity of the color-indicator end point, can be analyzed by an alternate test method (ASTM D-664). The quality of the mineral oil products renders them suitable for determination of the acid number.

The principle behind the acid number test is a holdover from earlier refining processes when it was believed, with some justification, that detectable amounts of chemicals that were used in refining could remain in the finished product (ASTM D-974, ASTM D-1093, IP 139). However, oxidation (ASTM D-943, ASTM D-3339, ASTM D-5770, IP 431) of various

oils during use or during storage can induce the formation of acidic species within the oil. Thus the occurrence of acidic entities within the oil is still a concern even though the reason may be different.

To determine the acid number (ASTM D-974), 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 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, with methyl orange as an indicator.

The total absence of organic acidity is never feasible, but a very low limit must be set if corrosion of copper (ASTM D-130, ASTM D-849, ASTM D-4048, ASTM D-4636, IP 154) and other components is to be avoided; moreover, more than a trace of some organic acids can adversely affect the response of the oil to amine inhibitors.

Similarly to the principle of acidic constituents, oil may, on occasion, contain alkaline or basic constituents. The presence of such constituents is determined through test methods for the base number. The relative amounts of these materials can be determined by titrating with acids.

Thus, in a manner akin to the *acid number*, the *base number* (often referred to as the *neutralization number*) is a measure of the basic constituents in the oil under the conditions of the test. The base number is used as a guide in the quality control of oil formulation and is also used as a measure of oil degradation in service.

There are four different test methods for the determination of base numbers (ASTM D-664, ASTM D-974, ASTM D-2896, ASTM D-4739). However, the different base number methods may give different results for the same sample.

If the mineral oil contains additives that react with alkali to form metal soaps, the saponification number (ASTM D-94, IP 136) expresses the amount of base that will react with 1 g of the sample when heated in a specific manner. Because compounds of sulfur, phosphorus, halogens, and certain other elements, which are sometimes added to petroleum products, also consume alkali and acids, the results obtained indicate the effect of these extraneous materials in addition to the saponifiable material present. In the test method, a known weight of the sample is dissolved in methyl ethyl ketone or a mixture of suitable solvents. It is heated with a known amount of standard alcoholic potassium hydroxide for between 30 and 90 min at 80°C (176°F). At the end of the reaction, the excess alkali is titrated with standard hydrochloric acid and the saponification number is calculated.

11.3.2. Aniline Point

The aniline point or mixed aniline point (ASTM D-611, IP 2) gives an indication of the hydrocarbon group composition of an oil. The lower the aniline point, the more aromatic the oil, and, for any particular compound type, the aniline point rises with molecular weight and with viscosity.

In the test, equal volumes of aniline and oil are mixed and heated until a miscible mixture is formed. During cooling at a prescribed rate, the temperature at which the mixture becomes cloudy is recorded and identified as the aniline point. Although not usually applicable to pharmaceutical grade mineral oils, the test is used in technical oil specifications as a measure of degree of refinement and type of base oil stock. For any particular oil fraction. a higher degree of refinement is reflected by an increase in aniline point. Aniline point also increases with the average molecular weight of the oil as well as with increasing proportions of paraffinic hydrocarbons to naphthenic hydrocarbons. Aniline point specifications also can be used to advantage for light technical grade mineral oils used in agricultural sprays, where the presence of aromatic hydrocarbons might cause floral damage.

For electrical oils the aniline point is often an indicator of the aromatic content because too high a value could give rise to oxidation instability and too low a value to inadequate gassing characteristics under electric stress. For these reasons an aniline point, usually in the form of a range of permitted values, is sometimes included in specifications. An increase in the aniline point after extraction with sulfuric acid is perhaps a better indication of aromatic content than the aniline point of the untreated sample.

The test for aniline point (ASTM D-611, IP 2) is not usually applied to medicinal oils, but some users of technical grades specify a minimum value. For oils of similar purity and viscosity a high aniline point denotes a more paraffinic, and hence less dense, oil than a lower aniline point; the desire for a high aniline point runs counter to the view that the higher the density the more preferable the oil if it is desired to make emulsions (e.g., hair cream) therefrom. Generally, the higher the aniline point the greater the stability of the oil but, on the other hand, a high aniline point sample may only indicate more extensive refining if comparisons are made on fractions of the same boiling range from the same crude oil. In addition, variations in aniline point may reflect changes in depth of refining as well as differences in hydrocarbon group composition for oils of same the viscosity but different origins.

11.3.3. Asphaltene Content (Insoluble Constituents)

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. Insofar as the asphaltene content gives an indication of the amount of coke that can be expected during exposure to thermal conditions (Speight, 2001; Speight and Ozum 2002), there is little need for the application of the test to mineral oil. Thus determination of the asphaltene content of mineral oil may be considered superfluous, but there may be an occasion when there is the need to determine the amount of insoluble constituents precipitated by the addition of a low-boiling hydrocarbon liquid to mineral oil.

In any of the methods for the determination of the asphaltene content, a sample 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 (Speight et al., 1984). 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.

Another method is designed to remove pentane-insoluble constituents by membrane filtration (ASTM D-4055). In this method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer any particulates onto the filter, after which the filter (with particulates) is dried and weighed to give the pentane-insoluble constituents as a percentage by weight of the sample.

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 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 precipitating 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.

11.3.4. Carbonizable Substances (Acid Test)

Medicinal oil requires a test in which the reaction of the oil to hot, strong sulfuric acid is used to determine the presence of carbonizable substance in the oil. However, the test for carbonizable substances (ASTM D-565)

should not be confused with the test methods for determining *carbon residue* (ASTM D-189, ASTM D-524, ASTM D4530, IP 13, IP 14, IP 398).

In the test method (ASTM D-565), the mineral oil is treated with concentrated sulfuric acid under prescribed conditions and the resulting color is compared with a reference standard to determine whether it passes or fails the test. When the oil layer shows no change in color and when the acid layer is not darker than the reference standard colorimetric solution, the oil is reported as passing the test. A bluish haze or a slight pink or yellow color in the oil layer should not be interpreted as a change in color. This is a pass-fail, and the more fully refined the oil, the lighter the color of the acid layer.

With the introduction of ultraviolet absorption procedures (ASTM D-2008, ASTM D-2269), the test finds less use but still provides a useful method to determine possible contamination of mineral oil with impurities transparent to both visible and ultraviolet light and hence not detectable by color or by ultraviolet absorption measurements.

For technical mineral oils the test for unsulfonatable residue (ASTM D-483) may be applied, but the test is of less significance for mineral oil that is refined to medicinal standard. The other quality criteria are much more stringent, and the test method for unsulfonatable residue does not have the required sensitivity.

11.3.5. Carbon Residue

Mineral oils are usually considered to have a high propensity for carbon formation and deposition under thermal conditions. Nevertheless, the tests that are applied to determine the carbon-forming propensity of fuel oil (and other petroleum products) are also available for application to mineral oils. The test methods for the carbon residue should not be confused with the test method for carbonizable substances (ASTM D-565). The former test methods are thermal in nature, whereas the latter test method involves the use of sulfuric acid in a search for specific chemical entities within the oil.

Thus the tests for Conradson carbon residue (ASTM D-189, IP 13), the 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 often included in inspection data for fuel oil.

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 D-524, 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 cracks 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 D-4530, IP 398) are equivalent to those produced by the Conradson carbon 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.

The data give an indication of the amount of constituents that may be undesirable in the oil, thereby requiring that the oil, depending on its designated use, be subjected to further refining.

Finally, a method that is used to determine pitch volatility (ASTM D-4893) might also be used, on occasion, to determine the nonvolatility of mineral oil. In the method, an aluminum dish containing about 15 g of accurately weighed sample is introduced into the cavity of a metal block heated and maintained at 350°C (662°F). After 30 min, during which the volatiles are swept away from the surface of the sample by preheated nitrogen, the residual sample is taken out and allowed to cool down in the desiccator. Nonvolatility is determined by the sample weight remaining and reported as % w/w residue.

11.3.6. Cloud Point

The *cloud point* is the temperature at which a cloud of wax crystal first appears in a liquid when it is cooled under conditions prescribed in the test method. This test method covers only petroleum oils that are transparent in layers 38 mm (1.5 in.) in thickness, and have a cloud point below 49°C (120°F). The cloud point is an indicator of the lowest temperature of the utility of an oil for certain applications, and it is usually higher than the pour point (ASTM D-97, ASTM D-5853, ASTM D-5949, ASTM D-5950, ASTM D-5985, IP 15).

The cloud point (ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP 219) is the temperature at which wax appears in an oil. This information is significant for oils to be used at low temperatures, where precipitation of wax might affect the performance of the oil.

In one of the tests (ASTM D-2500, IP 219), the oil is maintained at 0°C (32°F) for 4 h, when a 0.5-mm black line must be *easily seen* through an oil layer 25 mm thick. The setting of a value as low as this is dictated largely by considerations of appearance of the oil; a much higher temperature could well be tolerated if only practical considerations applied. Moreover the *n*-paraffins that are responsible for cloudiness (hence the need to observe that the opalescence is not due to moisture) are among the more inert of the hydrocarbon groups of which these mineral oils are composed.

The later test methods (ASTM D-5771, ASTM D-5772, ASTM D-5773) are alternative procedures that use automatic apparatus. However, when the specifications state that the original method (ASTM D-2500, IP 219) should be used, these later methods should not be applied without obtaining comparative data first. However, all three methods have a higher degree of precision than the original method.

Neither the cloud point nor the pour point should be confused or interchanged with the *freezing point* (ASTM D 2386, ASTM D-5901, ASTM D-5972, IP 16, IP 434, IP 435). The freezing point presents an estimate of minimum handling temperature and minimum line or storage temperature. It is not a test for an indication of purity and has limited value for mineral oil.

11.3.7. Color and Taste

By definition, pharmaceutical grade mineral oil must be colorless and transparent. Although the eye can determine color, it is usual to determine color by instrument.

The colorless character of these oils is important in some cases, because it may indicate the chemically inert nature of the hydrocarbon constituents. Textile lubricants should be colorless to prevent staining of light-colored threads and fabrics. Insecticide oils should be free of reactive (easily oxidized) constituents so as not to injure plant tissues when applied as sprays (ASTM D-483).

The main use of mineral oil in medicine has been as a laxative (an alimentary tract lubricant) and in various pharmaceutical preparations such as ointments, and, as such use continues, this quality of oil is finding increasing utilization as a lubricant for food processing machinery and in plastics manufacture. Laxative oils should be free of odor and taste and also be free of hydrocarbons that may react during storage and produce unwanted by-products. These properties are attained by the removal of oxygen-,

nitrogen-, and sulfur-containing compounds, as well as reactive hydrocarbons by, for example, sulfuric acid. The maximum permissible quantity of such oil traces is prescribed, but also the purity of the oil (ASTM D-2269) requires that the absorbance be measured on a dimethyl sulfoxide extract of the oil.

Determination of the color of mineral oil is used mainly for manufacturing control purposes and is an important quality characteristic. In some cases the color may serve as an indication of the degree of refinement of the material. However, color is not always a reliable guide to product quality and should not be used indiscriminately in product specifications (ASTM D-156, ASTM D-1209, ASTM D-1500, ASTM D-1544, ASTM D-6045, IP 17).

In one test (ASTM D-156) for the determination of color the height of a column of the oil is decreased by levels corresponding to color numbers until the color of the sample is lighter than that of the standard. The color number immediately above this level is recorded as the Saybolt color of the oil, and a color number of +25 corresponds to water mineral, whereas the minimum color intensity reading on this scale is expressed by +30, a value normally attained by mineral oils. In another test (IP 17), in which the measurements are performed with an 18-in. cell against color slides on a scale, a color of 1.0 or under is considered water-mineral and medicinal oils will normally be 0.5 or less. Conversion scales for different color tests are available (ASTM D-1500).

Although sometimes found in insulating oil specifications, the color characteristic is of no technical significance. Pale oils are, as a general rule, more severely refined than dark oils of the same viscosity, and color (ASTM D-1500, IP 17) is not a guide to stability. Deterioration of color after submission of the oil to an aging test is sometimes limited, but here again extent of oil deterioration can be much better measured by some other property such as acidity development or change in electrical conductivity (ASTM D-2624, ASTM D-4308, IP 274). About the only point that can be made in favor of color measurement on new oil is that it can give an immediate guide to a change in supply continuity.

11.3.8. Composition

The potential for the presence in mineral oil of trace amounts of carcinogenic polynuclear aromatic hydrocarbons cannot be overestimated. Thus compositional tests focus on the production of data relating to the presence of aromatic and polynuclear aromatic constituents in mineral oil.

As a result, a test method (ASTM D-2269) that can be applied to the ultraviolet absorbance of mineral oil is available. The investigation can be performed either directly on the oil itself (or on oil diluted with inert solvent) or else on a solvent extract of the oil, the solvent chosen (e.g.,

dimethyl sulfoxide) being one that will extract and concentrate the polynuclear aromatics.

Although informative, there have also been extensive efforts to correlate composition with physical properties. Among the most definitive of these efforts was the refractive index-density-molecular weight (n-d-M) method (ASTM D-3238). Carbon type composition gives the breakdown of total carbon atoms between various structures. Following from this, another method (ASTM D-2140, derived from n-d-M analysis (ASTM D-3238), involves the measurement of refractive index, density, and viscosity, for all of which standard procedures are available. From the data, it is possible to determine the distribution of carbon types (paraffin chains, naphthenic rings, and aromatic rings) in the oil. However, it is important to recognize that the percent aromatic carbon determined by this method does not correspond to *aromatics* as determined by other procedures (e.g., adsorption chromatography). For example, octadecylbenzene ($C_6H_5C_{18}H_{37}$) has only has 25% of the carbon as aromatic carbon (C_A) but chromatographic separation would show this compound to be separated as an aromatic compound.

Aniline point (ASTM D-611, IP 2) gives an indication of the hydrocarbon group composition of oil. The aniline point rises with molecular weight; also, for a given viscosity, the higher the aniline point the more paraffinic the oil. For electrical oils it is sometimes desirable to control the aromatic content because too high a value could give rise to oxidation instability and too low a value to inadequate gassing characteristics under electric stress. For these reasons an aniline point, usually in the form of a range of permitted values, is sometimes included in specifications. And a rise in the aniline point after extraction with sulfuric acid is perhaps a better indication of aromatic content than aniline point on the untreated sample.

A technique for applying infrared measurements to insulating oil is available (ASTM D-2144), and considerable information about mineral oil composition can be gained from infrared spectroscopy. Oxygenated bodies formed when oil deteriorates can be recognized, and hence this procedure can be used for surveillance of oils in service. An infrared spectrum can also give information as to the aromaticity of an oil and can detect antioxidants such as 2,6 di-tertiary butyl *p*-cresol. A chemical test for the latter is, however, available and is preferable for quantitative purposes (ASTM D-1473).

Although the total sulfur content (ASTM D-129, IP 61) of medicinal oil is not limited as such, it is in effect restricted (usually to well below 100 ppm) by the necessity of severe refining to meet the other clauses of the specification. However, the total sulfur content of mineral oils normally is well below 100 ppm because of the severe refining to which the oil has been subjected (Speight, 2000). Therefore, sulfur is not a limiting factor in the

specifications of mineral oil. Nevertheless, test methods are available to determine the presence of sulfur compounds in mineral oil, although the preferred procedure is often the Doctor test (ASTM D-4952, IP 30). For medicinal oils the procedure is that two drops of a saturated solution of lead monoxide in 20% aqueous sodium hydroxide are added to two volumes of oil and one volume of absolute ethyl alcohol. The mixture is heated to 70°C (158°F) for 10 min and should remain colorless.

Other test methods for the determination of corrosive sulfur (specifically hydrogen sulfide) are also available (ASTM D-6021, ASTM D-5705), which have been developed for residual fuel oil but can be applied to medicinal oil. Another test method (ASTM D-3227, IP 324) is used for the determination of mercaptan (R-SH) sulfur in petroleum products up to and including distillate fuels. However, there is no reason that the test could not be applied to mineral oil, with the use of any necessary modifications for solubility of the mineral oil in the alcoholic solution used for the titration.

In view of the wide use of copper in electrical equipment, it is essential to ensure that the oil does not corrode this metal. Noncorrosive or corrosive sulfur can be verified by any one of several test methods (ASTM D-130, ASTM D-849, ASTM D-4048, ASTM D-4636, IP 154) in which the oil is heated in the presence of a metallic copper strip for a specified time at a specified temperature after which the strip must be discolored. In addition, corrosiveness toward silver is becoming increasingly important, and a test method (IP 227) has been developed that is closely similar to the copper corrosion test.

Molecular type analysis separates an oil into different molecular species. A molecular type analysis is the so-called *clay-gel analysis*. In this method, group separation is achieved by adsorption in a percolation column with selected grades of clay and silica gel as the adsorption media (ASTM D-2007).

11.3.9. Density (Specific Gravity)

The use of density (specific gravity) data (ASTM D-1298, IP 160) for mineral oil is variable, although, for some grades of mineral oil, a high density can be indicative of the ultimate use of the oil.

For example, density or specific gravity data (ASTM D-1298, ASTM D-1480, ASTM D-1481, ASTM D-4052, ASTM D-5002 IP 160) are frequently included as a specification requirement for transformer oil when transformers operate in cold climates. Water, however undesirable in electrical equipment, does collect therein, and if an oil has a high density, any water/ice present would float on the oil instead of remaining at the bottom of the oil container, thereby reducing the effectiveness of the oil.

For heavier insulating oil, the purpose of limiting density range is to provide a check on oil composition. In addition, a minimum density may offer some indication of solvent power as well as guarding against excessive paraffin content. In this respect, the inclusion of density in a mineral oil specification may duplicate the aniline point (ASTM D-611, IP 2) requirement.

The API gravity (ASTM D-287) is a special function of specific gravity that was arbitrarily established to permit use of a wider industrial range of numbers and is derived from the specific gravity:

$$\text{API gravity, deg} = (141.5/\text{sp gr } 60/60°\text{F}) - 131.5$$

Density, specific gravity, and API gravity values permit conversion of volumes at the measured temperature to volumes at the standard petroleum temperatures of 15°C (60°F). Calculation of weight is possible where compositions are formulated on a weight basis. At a given viscosity, density, specific gravity, and API gravity provide a means for determining whether a mineral oil is derived from a paraffinic or a naphthenic feedstock.

11.3.10. Electrical Properties

Electrical properties of one form or another are included in virtually all specifications for insulating oils.

The *electric strength* or *dielectric breakdown* test method (ASTM D-877) indicates the absence, or presence, of free or suspended water and other contaminant matter that will conduct electricity. A high electric strength gives no indication of the *purity* of an oil in the sense of degree of refinement or the absence of most types of oil-soluble contaminants. This test method is of some assistance, when applied to an otherwise satisfactory oil, to indicate that the oil is free of contaminants of the type indicated above; in practice, this ensures that the oil is dry.

The test for stability (gas evolution) under electric stress must not be confused with tests for the gas content of insulating oil (ASTM D-831, ASTM D-1827, ASTM D-2945). These tests are largely factory control tests to ensure that oils intended for filling equipment have been adequately degassed (because dissolved gas, like gas evolved under stress, could cause void formation).

11.3.11. Flash Point and Fire Point

The flash point (closed tester: ASTM D-93/IP 34; open tester: ASTM D-92/IP 36) is the lowest temperature at atmospheric pressure (760 mmHg, 101.3 kPa) at which application of a test flame will cause the vapor of a

sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. Flash point data are used in shipping and safety regulations to define *flammable* and *combustible* materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively nonvolatile or nonflammable material. The fire point (ASTM D-92, IP 36) is the temperature at which the oil ignites and burns for 5 s.

Of the available test methods (ASTM, 2000), the most common method of determining the flash point confines the vapor (closed cup) until the instant the flame is applied (ASTM D-56, ASTM D-93, ASTM D-3828, ASTM D-6450, IP 34, IP 94, IP 303). An alternate method that does not confine the vapor (open cup method (ASTM D-92, ASTM D-1310, IP 36) gives slightly higher values of the flash point.

The flash point is sometimes to be found in a mineral oil specification, but the value is not usually of much significance and is merely laid down as some assurance against undue fire risk. Typical values will be from 150°C (302°F) upward, depending on viscosity. The closed test (IP 34) is commonly used, and a minimum value of 140°C (284°F) is required for transformer oil to limit fire risk. The stipulation of a suitable flash point also automatically limits the volatility of the oil, and for this reason the loss on heating (IP 46) can be important to restrict excessive volatility. This can be achieved by setting a suitable minimum flash point on the order of 125°C (257°F).

Fewer volatility problems arise with the heavier cable oils or oil-based cable impregnating compounds, although here also a minimum flash point of approximately 230°C (446°F) is frequently specified as a precaution against the presence of lighter (and hence undesirably volatile) components that could be troublesome at impregnating conditions of over 100°C (212°F) and high vacuum.

Rubber compounders often use flash point (ASTM D-92, IP 36, ASTM D 93, IP 34) as a measure of oil volatility. Volatility is important because rubber products are exposed to elevated temperatures during mixing operations and, often, in service. Although flash point has a certain utility for this purpose, it gives no indication of the amount of low-boiling material present. Therefore, a distillation curve should be used when volatility is a critical factor.

11.3.12. Interfacial Tension

The measurement of interfacial tension (ASTM D-971, ASTM D-2285) between oil and water is a sensitive method for determining traces of polar contaminants, including products of oil oxidation, and minimum values will sometimes be found in insulating oil specifications. The test is frequently

used to assess transformer oil deterioration and thus to maintain a check on the quality of oil in electrical equipment.

11.3.13. Iodine Value

The iodine number (iodine value) test method (ASTM D-2078, IP 84) is included in some specifications and is a measure of fatty acid components or unsaturation either as olefins and/or aromatics. The former are very unlikely to be present in any oil that has undergone sufficient refining to make it colorless, whereas the aromatic content can be controlled by setting a suitable value for the ultraviolet absorption.

In the test method (ASTM D-2078), a sample is dissolved in chloroform and reacted with Wijs solution for 30 min in the dark at 25°C. At the end of the reaction, the solution is mixed with potassium iodide (KI) and titrated with sodium thiosulfate and starch indicator and compared to a blank determination.

The bromine number is the number of grams of bromine that will react with 100 g of the sample under the test conditions and is better suited to the determination of unsaturated constituents in oil (ASTM D-875, ASTM D-1159, ASTM D-2710, IP 130). The magnitude of the bromine number is used as a measure of aliphatic unsaturation in petroleum products. In the test, a known weight of the sample dissolved in a specified solvent maintained at 0–5°C (32–41°F) is titrated with standard bromide-bromate solution. Determination of the end point is method dependent.

11.3.14. Oxidation Stability

Very many oxidation tests for transformer oils have been used at one time or another. Most of these tests are of a similar pattern: The oil is heated and subjected to oxidation by either air or oxygen and usually in the presence of a metallic catalyst, almost invariably copper, which is the main active metal in transformer construction. Temperatures and duration have varied within wide limits, from 95 to 150°C (203–302°F) and from 14 to 672 h.

In one test method (ASTM D-943), the oil is maintained at 100°C (212°F) for up to 1 week, during which time oxygen is passed through the oil, in which metallic copper is immersed. At the end of the oxidation period the amount of solid deterioration products (*sludge*) is measured, after such sludge has been precipitated by dilution of the aged oil with *n*-heptane, and the soluble (*acid*) decomposition products are also measured by determination of the neutralization value of the aged oil.

To shorten the time for the oxidation test method, a test for sludge formation in transformer oil by high-pressure oxidation bomb has been devel-

oped (ASTM D-1313) in which oxidation is carried out at 140°C (284°F) under pressurized oxygen for 24 h and the sludge formed is separated and weighed. A somewhat similar test, designed for inhibited oils, operates at the same temperature but lower pressure and employs a copper catalyst (ASTM D-2112).

One criticism of such tests is that sludge precipitation is carried out with *precipitation naphtha*. Although the characteristics of this mixture are defined, it is a complex hydrocarbon mixture whose composition can vary widely even within the range of prescribed properties. This could give rise to varying precipitation capabilities in various batches of such naphtha, a disadvantage that cannot occur when a pure chemical such as *n*-heptane is used as precipitant (ASTM D-3279, ASTM D-4124, IP 143). Another criticism is that the pressurized oxygen might be capable of changing the chemistry of the oxidation reaction and that the oxidation conditions do not represent the service conditions.

Although most transformer oil oxidation tests are of the air- or oxygen-blowing type, many methods of assessing cable oil deterioration depend on static oxidation, that is, the oil and air are in contact but such contact is not stimulated. A catalyst is sometimes, but not invariably, used. Thus, in the open beaker oxidative aging test (ASTM D-l934), the oil is exposed to moving air at 115°C (239°F) for 96 h but a metallic catalyst is optional. The metal is not specified, although copper is most frequently used in oxidation tests on insulating oils. Characteristics to be determined after aging are again left open in the test description, although acidity and electrical conductivity (both AC and DC) are the most common. Color is sometimes included, but the limited amount of information that this conveys has already been commented upon.

A transformer oil should not contain levels of unsaturated components (aromatics and/or olefins) that affect the oxidation resistance of the oil (ASTM D-2300). Another type of test (ASTM D-2298) exposes the degassed oil to electric stress, in a vacuum and at room temperature, the amount of gas evolved at the end of 1000 min being measured.

Acidity (ASTM D-974, IP 1, IP 139) after oxidation is another criterion by which the extent of oil deterioration is judged.

11.3.15. Pour Point

The pour point provides a means of determining the type of petroleum feedstock from which the mineral oil was manufactured or its previous processing history. It also reflects the presence of wax or paraffinic hydrocarbons. In any application in which the mineral oil is used at low temperatures or the oil is subjected during handling or storage to low temperatures, the pour point is important and, perhaps, even critical.

In the pour point test (ASTM D-97, IP 15), the oil is heated to a specified temperature that is dependent on the anticipated pour point range, cooled at a specified rate, and examined at 3°C (5°F) intervals for flow. The lowest temperature at which no movement of the oil is detected is recorded. The 3°C (5°F) temperature value immediately preceding the recorded temperature is defined as the pour point.

For the pour point of transformer oils, a value below the lowest ambient temperature to be expected must be set according to the specifications. Most oils have a pour point that is typically on the order of –40°C (–40°F).

11.3.16. Refractive Index

The refractive index (ASTM D-1218, ASTM D-1747) is the ratio of the velocity of light in air to its velocity in the substance under examination. It is used, together with density and viscosity measurements, in calculating the paraffin-naphthene ratio in mineral oils. Because refractive index is a measure of aromaticity and unsaturation on a given stock, manufacturers also use it as a means of process control.

The refractive index is also needed to calculate the refractivity intercept in the determination of carbon type composition (Speight, 2000).

11.3.17. Smoke Point

The smoke point is of particular interest to industries, such as the baking industry, whose processes expose or use mineral oil at extremely high temperatures.

The smoke point test (ASTM D-1322, IP 57), originally developed for kerosene, is conducted with an enclosed wick-fed lamp suitably vented and illuminated to permit detection of vapors. The oil is carefully heated under specified conditions until the first consistent appearance of vapors is detected. The temperature of the oil at that time is recorded as the smoke point. If necessary, this test can be adapted for use with mineral oil. The character of the flame is an indicator of the aromatics content.

11.3.18. Specific Optical Dispersion

The specific optical dispersion (ASTM D-1807) serves as an indication of aromatic content. The difference in refractive index of the oil as measured at two wavelengths is determined, divided by the relative density (all measurements are at the same temperature) and multiplied by 100; values above 97 are stated to bear a direct relationship to the aromatic content of the oil.

If, however, there is reason to be particularly interested in the aromatic content, it is preferable to assess this by one of the more direct methods.

11.3.19. Ultraviolet Absorption

Considerable concern has been generated in recent years over the possible presence of carcinogenic polynuclear aromatic hydrocarbons in mineral oils.

Detection of these chemicals by ultraviolet absorption spectroscopy (ASTM D-2269) measures the absorbance over the wavelength range of 260–350 nm in a 10-mm cell of a dimethyl sulfone extract of the oil. The polynuclear aromatic hydrocarbons present in the mineral oils are concentrated. In fact, the ultraviolet absorption level corresponds, approximately, to a maximum polynuclear aromatics content of about 5 ppm.

For oils of a similar type, ultraviolet (UV) absorptivity is a good indicator of the resistance of an oil to discoloration under exposure to artificial or natural light. Oils with low absorptivity at 260 nm have been found to impart good color stability to light-colored rubber compounds (ASTM D-2008).

11.3.20. Viscosity

Viscosity (ASTM D-445, IP 71) is one of the most important properties to be considered in the evaluation of a mineral oil.

Requirements for viscosity vary widely according to the user for which the oil is intended and may be as low as 4 cSt or as high as 70 cSt. Mineral oil for internal use generally should have high viscosity to minimize possibilities of leakage.

Viscosity data (ASTM D-445, IP 71) are used to ensure that, in the case of oils for internal use as laxatives, unduly fluid material, which could increase risk of leakage through the anal sphincter muscle, is not used. The minimum viscosity is usually on the order of 75 cSt at 37.8°C (100°F). The temperature of viscosity measurement is a normal one employed for this purpose and happens, in the case of medicinal oils, to be that of the human body. Thus the viscosity of these oils is measured at their working temperature.

Heavy cable oils are very much more viscous materials, and typical viscosity values can be as high as about 200 cSt at 60°C (140°F). Such oils are probably the only petroleum products for which a maximum viscosity index (ASTM D-227, IP 226) is sometimes specified, to ensure that, although the oil will be as fluid as possible at impregnating temperatures (100°C/212°F or more), it will be sufficiently viscous to prevent draining at ambient temperatures in cases where cables are laid on a steep gradient.

The viscosity-gravity constant (ASTM D-2501) and the refractivity intercept (r) have been used for characterizing oils of widely different viscosity (ASTM D-2140).

11.3.21. Volatility

The distillation range for very mineral light oils provides information on volatility, evaporation rates, and residue remaining after evaporation (ASTM D-86, ASTM D-1160, IP 123).

Such data are important for agricultural and household sprays, agricultural product processing, and printing inks. The baking and plastic industries often include initial boiling point temperature, the minimum allowable temperature at which the first several percent of the oil comes overhead during distillation, or both as part of their specifications for mineral oils.

The test for evaporation (ASTM D-972) gives a measure of oil volatility under controlled conditions and is used frequently for specification purposes. However, because volatility of oil from a rubber compound may be influenced by its compatibility with the rubber, a volatility test of the compound often is made under laboratory test conditions pertinent to the intended service.

11.3.22. Water

Water is obviously undesirable in electrical equipment, and the water content of transformer and other insulating oils is frequently limited to a low maximum value. Traces of water that would not influence the general run of petroleum product tests could have a very significant effect on properties such as electric strength.

Quantitative determination may be made by one of the many modifications of the Karl Fischer method (ASTM D-l533). With careful application of this technique, using electrical methods of determining the end point and operating in a sealed system, water can be determined down to about 2 ppm or even less. Such sensitivity is, however, rather greater than is normally required, and a water content of 35 ppm and preferably less than say 25 ppm is usually considered satisfactory. The solubility level of water in oil at room temperature (say 20°C/68°F) will vary with the type of oil but is around 40 ppm. Amounts of water down to about 5 ppm, in addition to being measurable chemically, can also be determined by removing the water from the oil by a combination of heat and vacuum and absorbing the freed moisture in a suitable weighed phosphorus pentoxide (P_2O_5) trap.

11.3.23. Wax Appearance Point

The *wax appearance point* is the temperature at which wax begins to precipitate (hence it is also called the *wax precipitation point*) from an oil under specified cooling conditions. Although more applicable to distillate fuel oil, the wax appearance point can also have implications for mineral oil use. In

the test method (ASTM D-3117), a sample of the oil is cooled under prescribed conditions with stirring. The temperature at which wax first appears is the wax appearance point.

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CHAPTER

12

LUBRICATING OIL

12.1. INTRODUCTION

Lubricating oil is used to reduce friction and wear between bearing metallic surfaces that are moving with respect to each other by separating the metallic surfaces with a film of the oil. Lubricating oil is distinguished from other fractions of crude oil by a high (>400°C/>750°F) boiling point (Table 12.1, Figure 12.1) (Gruse and Stevens, 1960; Guthrie, 1967; Berkley, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Warne, 1998; Speight, 2000; Banaszewski and Blythe, 2000).

In the early days of petroleum refining, kerosene was the major product, followed by paraffin wax wanted for the manufacture of candles. Lubricating oils were at first by-products of paraffin wax manufacture. The preferred lubricants in the 1860s were lard oil, sperm oil, and tallow, but as the trend to heavier industry increased, the demand for mineral lubricating oils increased, and after the 1890s petroleum displaced animal and vegetable oils as the source of lubricants for most purposes.

12.2. PRODUCTION AND PROPERTIES

Lubricating oil is a mixture that is produced by distillation, after which chemical changes may be required to produce the desired properties in the product. One such property requires that the oil adhere to metal surfaces and ensure protection of moving parts by preventing metal-metal contact (ASTM D-2510).

Petroleum base lubricating oils are present in the atmospheric residuum (boiling above 370°C/698°F) of selected paraffinic and naphthenic crude oils. The production of lubricating oils is well established (Sequeira, 1992; Speight, 2000) and consists of five basic procedures:

1. Distillation and deasphalting to remove the lighter constituents of the feedstock.

Table 12.1. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

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

2. Solvent refining and/or hydrogen treatment to remove the non-hydrocarbon constituents and to improve the feedstock quality.
3. Dewaxing to remove the wax constituents and improve the low-temperature properties.
4. Clay treatment or hydrogen treatment to prevent instability of the product.

Lubricating oil manufacture was well established by 1880, and the method depended on whether the crude petroleum was processed primarily for kerosene or for lubricating oils. Usually the crude oil was processed for kerosene, and primary distillation separated the crude into three fractions, naphtha, kerosene, and a residuum. To increase the production of kerosene the cracking distillation technique was used, and this converted a large part of the gas oils and lubricating oils into kerosene. The cracking reactions also produced coke products and asphaltlike materials, which gave the residuum a black color; hence it was often referred to as *tar* (Speight, 2000; Speight and Ozum, 2002).

If the crude oil used for the manufacture of lubricating oils contained asphalt, it was necessary to acid treat the steam-refined oil before cold settling. Acid-treated, settled steam-refined stock was widely used as steam cylinder oils.

The development of vacuum distillation led to a major improvement in both paraffinic and naphthenic (low cold test) oils. By vacuum distillation the more viscous paraffinic oils (even oils suitable for bright stocks) could

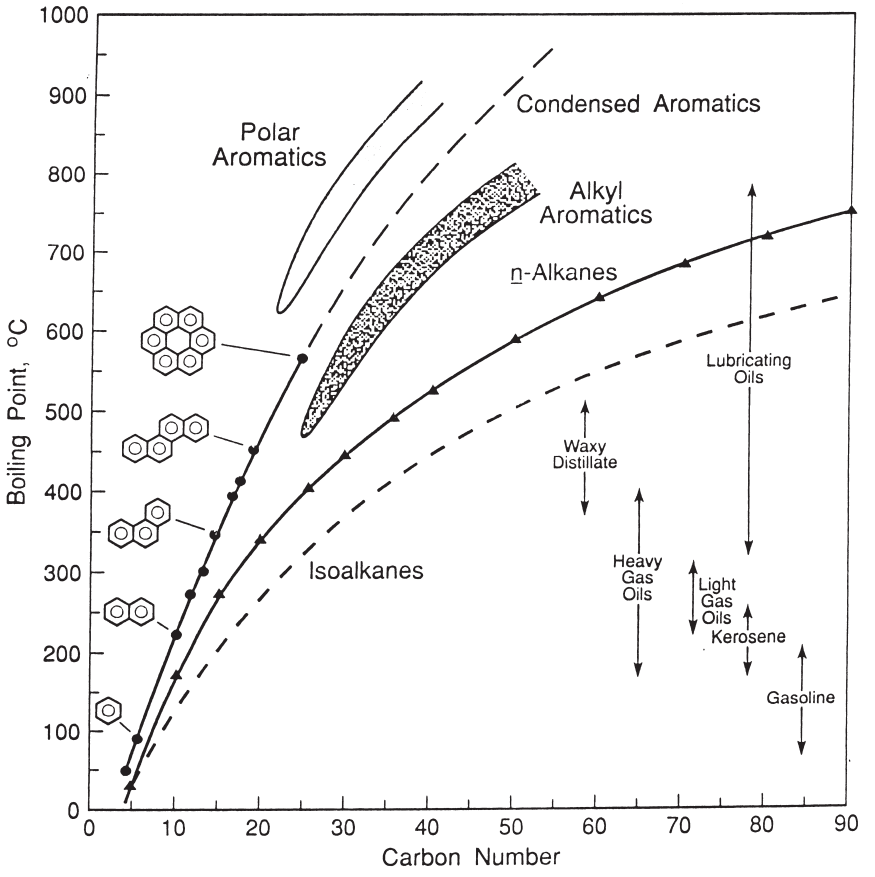

Figure 12.1. Boiling point and carbon number for various hydrocarbons and petroleum products

be distilled overhead and could be separated completely from residual asphaltic components. Vacuum distillation provided the means of separating more suitable lubricating oil fractions with predetermined viscosity ranges and removed the limit on the maximum viscosity that might be obtained in a distillate oil.

Materials suitable for the production of lubricating oils are comprised principally of hydrocarbons containing from 25 to 40 carbon atoms per molecule, whereas residual stocks may contain hydrocarbons with 50–60 or more (up to ~80) carbon atoms per molecule. The composition of a lubricating oil may be substantially different from that of the lubricant fraction from which it was derived, because wax (normal paraffins) is removed by distillation or refining by solvent extraction and adsorption preferentially

removes non-hydrocarbon constituents as well as polynuclear aromatic compounds and the multiring cycloparaffins.

There are general indications that the lubricant fraction contains a greater proportion of normal and branched paraffins than the lower-boiling portions of petroleum. For the polycycloparaffins, a good proportion of the rings appear to be in condensed structures and both cyclopentyl and cyclohexyl nuclei are present. The methylene groups appear principally in unsubstituted chains at least four carbon atoms in length, but the cycloparaffin rings are highly substituted with relatively short side chains.

Mono-, di-, and trinuclear aromatic compounds appear to be the main constituents of the aromatic portion, but material with more aromatic nuclei per molecule may also be present. For the dinuclear aromatics, most of the material consists of naphthalene types. For the trinuclear aromatics, the phenanthrene type of structure predominates over the anthracene type. There are also indications that the greater part of the aromatic compounds occur as mixed aromatic-cycloparaffin compounds.

In the majority of cases, chemical additives are used to enhance the properties of base oils to improve such characteristics as oxidation resistance (ASTM D-2893, ASTM D-4742, ASTM D-5846) change in viscosity (ASTM D-445, IP 71) with temperature, low-temperature flow properties as derived from the pour point (ASTM D-97, ASTM D-5853, ASTM D-5949, ASTM D-5950, ASTM D-5985, IP 15) and fluidity measurements (ASTM D-6351), emulsifying ability (ASTM D-2711), extreme pressure (ASTM D-2782, ASTM D-2783, ASTM D-3233, IP 240), antiwear and frictional properties (ASTM D-5183, ASTM D-6425), and corrosion resistance (ASTM D-4636). The selection of components for lubricating oil formulation requires knowledge of the most suitable crude sources for the base oils, the type of refining required, the types of additive necessary, and the possible effects of the interactions of these components on the properties of the finished lubricating oil.

Lubricating oils may be divided into many categories according to the types of service they are intended to perform. However, there are two main groups: (1) oils used in intermittent service, such as motor and aviation oils, and (2) oils designed for continuous service, such as turbine oils. Thus the test methods must be designed and applied accordingly.

This classification is based on the Society of Automotive Engineers (SAE) J 300 specification. The single-grade oils (e.g., SAE 20, etc.) correspond to a single class and must be selected according to engine manufacturer specifications, operating conditions, and climatic conditions. At –20°C (–68°F) a multigrade lubricating oil such as SAE 10W-30 possesses the viscosity of a 10W oil, and at 100°C (212°F) the multigrade oil possesses the viscosity of a SAE 30 oil.

Oils used in intermittent service must show the least possible change in viscosity with temperature; that is, their viscosity indexes must be high.

These oils must be changed at frequent intervals to remove the foreign matter collected during service. The stability of such oils is therefore of less importance than the stability of oils used in continuous service for prolonged periods without renewal. On the other hand, oils used in continuous service must be extremely stable, but their viscosity indexes may be low because the engines operate at fairly constant temperature without frequent shutdown and thermal stability (ASTM D-2070, ASTM D-2511, ASTM D-6205) is an important property.

12.3. TEST METHODS

The number of tests applied for product character and quality varies with the complexity of the product and the nature of the application. The more important tests, such as viscosity, flash point, and color are usually performed on every batch. Other tests may be on a statistical (or as-needed) basis dependent on data that can be presented in the graphical form of a *fingerprint* that is specific for the blend of components and additives in a particular formulation. Comparison of the fingerprint with a known standard can be used as a check on the composition.

12.3.1. Acidity and Alkalinity

Unused and used petroleum products may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products (ASTM D-5770). The relative amount of these materials can be determined by titrating with bases. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

Thus the acid number is a measure of this amount of acidic substance in the oil, always under the conditions of the test. Because a variety of oxidation products contribute to the acid number and the organic acids vary widely in corrosion properties, the test cannot be used to predict corrosiveness of an oil under service conditions.

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 with *p*-naphtholbenzein indicator solution (ASTM D-974, IP 139). However, many higher-molecular-weight oil products (dark-colored oils) that cannot be analyzed for acidity because of obscurity of the color-indicator end point can be analyzed by an alternate test method (ASTM D-664). The quality of the mineral oil products renders them suitable for determination of the acid number.

In a manner akin to the acid number, the *base number* (often referred to as the *neutralization number*) is a measure of the basic constituents in the oil under the conditions of the test. The base number is used as a guide in the quality control of oil formulation and is also used as a measure of oil degradation in service.

The *neutralization number*, expressed as the *base number*, is a measure of this amount of basic substance in the oil, always under the conditions of the test. The neutralization number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service; however, any condemning limits must be empirically established.

Samples of oil drawn from the crankcase can be tested to assess the reserve of alkalinity remaining by determining the total base number of the oil (ASTM D-664, ASTM D-2896, ASTM D-4739, IP 177, IP 276). Essentially, these are titration methods in which, because of the nature of the used oil, an electrometric instead of a color end point is used. The reserve alkalinity neutralizes the acids formed during combustion. This protects the engine components from corrosion. However, the different base number methods may give different results for the same sample.

Lubricating oil often contains additives that react with alkali to form metal soaps, and the *saponification number* expresses the amount of base that will react with 1 g of the sample when heated in a specific manner. In the test method (ASTM D-94, IP 136), a known weight of the sample is dissolved in methyl ethyl ketone or a mixture of suitable solvents and the mixture is heated with a known amount of standard alcoholic potassium hydroxide for between 30 and 90 min at 80°C (176°F). The excess alkali is titrated with standard hydrochloric acid, and the saponification number is calculated. The results obtained indicate the effect of extraneous materials in addition to the saponifiable material present.

12.3.2. Ash

The ash formed by the combustion of lubricating oil (ASTM D-482, ASTM D-2415, IP 4) is, as defined for other products, the inorganic residue, free from carbonaceous matter, remaining after ignition in air of the residual fuel oil at fairly high temperatures. The ash content is not directly equated to mineral content but can be converted to mineral matter content by the use of appropriate formulae.

12.3.3. Asphaltene Content (Insoluble Constituents)

The asphaltene fraction (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. Insofar as the asphaltene content gives an indication of the amount of coke that can be expected during exposure to thermal conditions (Speight, 2000; Speight, 2001, Speight and Ozum 2002), there is little need for the application of the test to lubricating mineral oil. Use of the oil under stressful conditions where heat is generated may introduce the need to determine the amount of insoluble constituents precipitated by the addition of a low-boiling hydrocarbon liquid to mineral oil.

Pentane-insoluble constituents can be determined by membrane filtration (ASTM D-4055). In this method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer any particulates onto the filter, after which the filter (with particulates) is dried and weighed to give the pentane-insoluble constituents as a percentage by weight of the sample.

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 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 precipitating 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.

On the other hand, if the lubricating oil has been subjected to excessive heat, it might be wise to consider application of the test method for determining the toluene-insoluble constituents of tar and pitch (ASTM D-4072, ASTM D-4312). In these methods, a sample is digested at 95°C (203°F) for 25 min and then extracted with hot toluene in an alundum thimble. The extraction time is 18 h (ASTM D-4072) or 3 h (ASTM D-4312). The insoluble matter is dried and weighed. Combustion will then show whether the material is truly carbonaceous or it is inorganic ash from the metallic constituents (ASTM D-482, ASTM D-2415, ASTM D-4628, ASTM D-4927, ASTM D-5185, ASTM D-6443, IP 4).

Another method (ASTM D-893) covers the determination of pentane- and toluene-insoluble constituents in used lubricating oils. Pentane-insoluble constituents include oil-insoluble materials, some oil-insoluble resinous matter originating from oil or additive degradation, or both. Toluene-insoluble constituents can come from external contamination, fuel carbon, highly carbonized materials from degradation of fuel, oil, and additives, or

engine wear and corrosion materials. A significant change in pentane- or toluene-insoluble constituents and insoluble resins indicates a change in oil that could lead to lubrication problems. The insoluble constituents measured can also assist in evaluating the performance characteristics of a used oil or in determining the cause of equipment failure.

Two test methods are used: Procedure A covers the determination of insoluble constituents without the use of coagulant in the pentane and provides an indication of the materials that can be readily separated from the oil-solvent mixture by centrifugation. Procedure B covers the determination of insoluble constituents in lubricating oil that contains detergents and uses a coagulant. In addition to the materials separated by using procedure A, this coagulation procedure separates some finely divided materials that may be suspended in the oil. The results obtained by procedures A and B should not be compared because they usually give different values. The same procedure should be applied when comparing results obtained periodically on an oil in use, or when comparing results determined in different laboratories.

In procedure A, a sample is mixed with pentane and centrifuged, after which the oil solution is decanted and the precipitate is washed twice with pentane, dried, and weighed. For toluene-insoluble constituents, a separate sample of the oil is mixed with pentane and centrifuged. The precipitate is washed twice with pentane, once with toluene-alcohol solution, and once with toluene. The insoluble material is then dried and weighed. In procedure B, procedure A is followed except that instead of pentane, a pentane-coagulant solution is used.

12.3.4. Carbonizable Substances (Acid Test)

The test for carbonizable substances with sulfuric acid is not usually applied to lubricating oil requirements. However, the need may arise and being aware of the availability of such a test is warranted. In this test method (ASTM D-565), a sample of the oil is treated with concentrated sulfuric acid under prescribed conditions and the resulting color is compared with a reference standard to determine whether it passes or fails the test. When the oil layer shows no change in color and when the acid layer is not darker than the reference standard colorimetric solution, the oil is reported as passing the test. A bluish haze or a slight pink or yellow color in the oil layer should not be interpreted as a change in color. The more fully refined the oil, the lighter the color of the acid layer.

However, with the introduction of ultraviolet absorption procedures (ASTM D-2008, ASTM D-2269), the test finds less use but still provides a useful method to determine possible contamination of lubricating oil with impurities transparent to both visible and ultraviolet light and hence not

detectable by color or by ultraviolet absorption measurements (ASTM D-2008).

The test for carbonizable substances (ASTM D-565) should not be confused with the test methods for determining *carbon residue* (ASTM D-189, ASTM D-524, ASTM D4530, IP 13, IP 14, IP 398) (q.v.).

12.3.5. Carbon Residue

Lubricating oil is not usually considered to be used under the extreme conditions under which coke is formed from, for example, fuel oil. Nevertheless, the tests that are applied to determine the carbon-forming propensity of fuel oil (and other petroleum products) are also available for application to lubricating oil should the occasion arise.

Thus the tests for the Conradson carbon residue (ASTM D-189, IP 13), the Ramsbottom carbon residue (ASTM D-524, IP 14), and the microcarbon carbon residue (ASTM D4530, IP 398) are often included in inspection data for fuel oil.

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 D-524, 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 cracks 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 D-4530, 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 D-4530, IP 398) are equivalent to those by the Conradson carbon method (ASTM D-189, IP 13). However, the 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.

12.3.6. Cloud Point

The *cloud point* is the temperature at which a cloud of wax crystal first appears in a liquid when it is cooled under conditions prescribed in the test method. This test method covers only petroleum oils that are transparent in layers 38 mm (1.5 in.) in thickness and have a cloud point below 49°C (120°F). The cloud point is an indicator of the lowest temperature of the utility of an oil for certain applications and it is usually higher than the pour point (ASTM D-97, ASTM D-5853, ASTM D-5949, ASTM D-5950, ASTM D-5985, IP 15).

The cloud point (ASTM D-2500, IP 219) of lubricating oil is the temperature at which paraffinic wax, and other components that readily solidify, begin to crystallize out and separate from the oil under prescribed test conditions. It is of importance to know when narrow clearances might be restricted by accumulation of solid material (for example, oil feed lines or filters).

Neither the cloud point nor the pour point should be confused or interchanged with the *freezing point* (ASTM D-D 2386, ASTM D-5901, ASTM D-5972, IP 16, IP 434, IP 435). The freezing point presents an estimate of minimum handling temperature and minimum line or storage temperature. It is not a test for an indication of purity and has limited value for lubricating oil.

12.3.7. Color

Determination of the color of petroleum products is used mainly for manufacturing control purposes and is an important quality characteristic. In some cases the color may serve as an indication of the degree of refinement of the material. However, color is not always a reliable guide to product quality and should not be used indiscriminately in product specifications (ASTM D-156, ASTM D-1209, ASTM D-1500, ASTM D-1544, ASTM D-6045, IP 17).

In one test (ASTM D-156) for the determination of color, the height of a column of the oil is decreased by levels corresponding to color numbers until the color of the sample is lighter than that of the standard. The color number immediately above this level is recorded as the Saybolt color of the oil, and a color number of +25 corresponds to water-mineral, whereas the minimum color intensity reading on this scale is expressed by +30, a value normally attained by mineral oils. In another test (IP 17), in which the measurements are performed with an 18-in. cell against color slides on a scale, a color of 1.0 or under is considered water-mineral and medicinal oils will normally be 0.5 or less. Conversion scales for different color tests are available (ASTM D-1500).

Although sometimes found in insulating oil specifications, the color characteristic is of no technical significance. Pale oils are, as a general rule, more severely refined than dark oils of the same viscosity, and color (ASTM D-1500, IP 17) is not a guide to stability. Deterioration of color after submission of the oil to an aging test is sometimes limited, but here again extent of oil deterioration can be much better measured by some other property such as acidity development or change in electrical conductivity (ASTM D-2624, ASTM D-4308, IP 274). About the only point that can be made in favor of color measurement on new oil is that it can give an immediate guide to a change in supply continuity.

12.3.8. Composition

The importance of composition of lubricating oils lies in the effect it has on their compatibility (ASTM D-2226). This can often be determined by studies of the composition. For example, molecular type analysis separates an oil into different molecular species. One molecular type analysis is the so-called *clay-gel analysis*. In this method, group separation is achieved by adsorption in a percolation column with selected grades of clay and/or silica gel as the adsorption media (ASTM D-1319, ASTM D-2007, IP 156).

Mass spectrometry can also be used for compositional studies of lubricating oil (ASTM D-3239). This test method covers the determination by high ionizing voltage, low-resolution mass spectrometry of 18 aromatic hydrocarbon types and three aromatic thiophene types in straight-run aromatic petroleum fractions boiling within the range from 205 to 540°C (400–1000°F). Samples must be nonolefinic, must not contain more than 1 mass % of total sulfur, and must not contain more than 5% nonaromatic hydrocarbons. The relative abundances of seven classes of aromatics in petroleum fractions are determined by using a summation of peaks most characteristic of each class. Calculations are carried out by the use of an inverted matrix derived from the published spectra of pure aromatic compounds. The aromatic fraction needed for this analysis is obtained by using liquid elution chromatography (ASTM D-2549).

Aromatic content is a key property of hydrocarbon oils insofar as the aromatic constituents can affect a variety of properties. An existing method using high-resolution nuclear magnetic resonance (ASTM D-5292) is applicable to a wide range of petroleum products that are completely soluble in chloroform and carbon tetrachloride at ambient temperature. The data obtained by this method can be used to evaluate changes in aromatic contents of hydrocarbon oils resulting from process changes. This test method is not applicable to samples containing more than 1% by weight olefinic or phenolic compounds. The hydrogen magnetic resonance spectra are obtained on sample solutions in either chloroform or carbon tetrachloride

with a continuous wave or pulse Fourier transform high-resolution nuclear magnetic resonance spectrometer. Carbon magnetic resonance spectra are obtained on the sample solution in deutero-chloroform with a pulse Fourier transform high-resolution nuclear magnetic resonance spectrometer.

The total quantity of sulfur in a gear oil due to the base oil and the additives present can be determined by a bomb method (ASTM D-129, IP 61) in which the sulfur is assessed gravimetrically as barium sulfate. The copper strip test (ASTM D-130, ASTM D-849, ASTM D-2649, IP 154) is used to simulate the tendency of the oil to attack copper, brass, or bronze. Because active sulfur is desirable for some extreme-pressure applications, a positive copper strip result can indicate that the formulation is satisfactory, but care is necessary in the interpretation of copper strip results because formulations of different chemical compositions may give different results and yet have similar performance in the intended application. Corrosion preventative properties are also measurable (ASTM D-4636).

The constituent elements (barium, calcium, magnesium, tin, silica, zinc, aluminum, sodium, and potassium) of new and used lubricating oils can also be determined (ASTM D-811). Corresponding methods for barium, calcium, and zinc in unused oils are available (IP 110, IP 111, and IP 117, respectively. For new lubricating oils ASTM D-874/IP 163 can be used to check the concentration of metallic additives present by measuring the ash residue after ignition. This latter method is useful to check the quality of new oils at blending plants or against specifications.

The lead content of new and used gear oils can be determined by the chemical separation method (IP 120). However, there are a number of instrumental techniques that enable the results to be obtained very much more rapidly, among which are polarographic, flame photometric, and X-ray fluorescence methods. Chlorine can be determined by a chemical method as silver chloride (ASTM D-808) or by a titration method (ASTM D-1317, IP 118).

Phosphorus can serve as a beneficial adjunct or as a deleterious agent. There are several test methods for the determination of phosphorus. In addition to the three test methods described here, reference should also be made to multielement analysis methods such as inductively coupled plasma atomic emission spectroscopy (ICPAES) (ASTM D-4951, ASTM D-5185) and X-ray fluorescence (XRF) (ASTM D-4927, ASTM D-6443) described above in this guide. Phosphorus can also be determined by a photometric procedure (IP 148) or by a test method (ASTM D-1091) in which the organic material in the sample is destroyed, phosphorus in the sample is converted to phosphate ion by oxidation with sulfuric acid, nitric acid, and hydrogen peroxide, and the magnesium pyrophosphate is determined gravimetrically. Another method (ASTM D-4047, IP 149) in which the phosphorus is converted to quinoline phosphomolybdate is also available.

The extent and nature of the contamination of a used automotive engine oil by oxidation and combustion products can be ascertained by determining the amounts of materials present in the lubricating oil that are insoluble in *n*-pentane and toluene (ASTM D-893).

In this test, a solution of the used lubricating oil in pentane is centrifuged, the oil solution is decanted, and the precipitate is washed, dried and weighed. Insoluble constituents (precipitate) are expressed as a percentage by weight of the original amount of used oil taken and include the resinous material resulting from the oxidation of the oil in service, together with the benzene-insoluble constituents. The latter are determined on a separate portion of sample that is weighed, mixed with pentane, and centrifuged. The precipitate is washed twice with pentane, once with benzene-alcohol solution, and once with benzene. The insoluble material is then dried and weighed to give the percentage of benzene insoluble constituents that contain wear debris, dirt, carbonaceous matter from the combustion products, and decomposition products of the oil, additives, and fuel.

Where highly detergent/dispersant oils are under test, coagulated pentane-insoluble constituents and coagulated benzene-insoluble constituents may be determined by using methods similar to those just described but employing a coagulant to precipitate the very finely divided materials that may otherwise be kept in suspension by the detergent/dispersant additives.

Size discrimination of insoluble matter may be made to distinguish between finely dispersed, relatively harmless matter and the larger, potentially harmful particles in an oil (ASTM D-4055). The method uses filtration through membranes of known pore size. Membrane filtration techniques are increasingly being used.

The metallic constituents (barium, boron, calcium, magnesium, tin, silicon, zinc, aluminum, sodium, potassium, etc.) of new and used lubricating oils can be determined by a comprehensive system of chemical analysis (ASTM D-874, IP 163).

Turbine oil systems usually contain some free water as a result of steam leaking through glands and then condensing. Marine systems may also have salt water present because of leakage from coolers. Because of this, rust inhibitors are usually incorporated. The rust-preventing properties of turbine oils are measured by a method (ASTM D-665, IP 135) that uses synthetic seawater or distilled water in the presence of steel. The oil should also be noncorrosive to copper (ASTM D-130, IP 154).

The presence of water in turbine systems tends to lead to the formation of emulsions and sludge containing water, oil, oil oxidation products, rust particles, and other solid contaminants that can seriously impair lubrication. The lubricating oil, therefore, should have the ability to separate from water readily and to resist emulsification during passage of steam into the oil until

a predetermined volume has condensed, and the time required for separation is measured (IP 19). Alternatively, the rate of separation of oil that has been stirred with an equal volume of water is measured (ASTM D-1401). These test methods are only approximate guides to the water-separating characteristics of modern inhibited turbine oils, and the results should be used in conjunction with experience gained of the particular service conditions encountered.

Although systems should be designed to avoid entrainment of air in the oil, it is not always possible to prevent this (ASTM D-892, IP 146). The formation of a stable foam (ASTM D-892, ASTM D-3519, ASTM D-3601, ASTM D-6082, IP 146) increases the surface area of the oil that is exposed to small bubbles of air, thus assisting oxidation. The foam can also cause loss of oil from the system by overflow. Defoaming agents are usually incorporated in turbine oils to decrease their foaming tendency. Air release is also an important property if a soft or spongy governor system is to be avoided. A careful choice of type and amount of defoaming agent will provide the correct balance of foam protection and air release properties.

Dilution of an oil by fuel under low-temperature or short-distance stop-start operation can occur frequently. Dilution of engine oil by diesel fuel can be estimated from gas chromatography (ASTM D-3524), and gasoline dilution can also be measured by gas chromatography (ASTM D-3525).

Low-temperature service conditions may also result in water vapor from combustion products condensing in the crankcase (ASTM D-95, IP 74).

12.3.9. Density (Specific Gravity)

There are alternative but related means of expressing the weight of a measured volume of a product.

Both density (specific gravity) and API gravity measurements are used as manufacturing control tests and, in conjunction with other tests, are also used for characterizing unknown oils because they correlate approximately with hydrocarbon composition and, therefore, with the nature of the crude source of the oil (ASTM D-l298, IP 160).

For lubricating oil, the purpose of limiting density range is to provide a check on oil composition. In addition, a minimum density may offer some indication of solvent power as well as guarding against excessive paraffin content. In this respect, the inclusion of density in a mineral oil specification may duplicate the aniline point (ASTM D-611, IP 2) requirement.

The API gravity (ASTM D-287, IP 192) is also used for lubricating oil and is based on a hydrometer scale that may be readily converted to a relative density basis by use of tables or formulae (Chapter 2):

$$\text{API gravity, deg} = (141.5/\text{sp gr } 60/60^\circ\text{F}) - 131.5$$

API density is also a critical measure reflecting the quality of lubricating oil.

12.3.10. Flash Point and Fire Point

The *flash point* gives an indication of the presence of volatile components in an oil and is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a flammable mixture with air.

The *fire point* is the temperature to which the product must be heated under the prescribed test conditions to cause the vapor-air mixture to burn continuously on ignition. The Cleveland open cup method (ASTM D-92, IP 36) can be used to determine both flash and fire points of lubricating oils, and the Pensky–Martens closed (ASTM D-93, IP 34) and open (IP 35) flash points are also widely used.

The flash and fire points are significant in cases where high-temperature operations are encountered, not only because of the hazard of fire but also as an indication of the volatility of an oil. In the case of used oils, the flash point is used to indicate the extent of contamination with more volatile oils or with fuels such as gasoline (ASTM D-3607). The flash point can also be used to assist in the identification of different types of base oil blend.

For used automotive engine oils that can be contaminated by a variety of materials, the presence of diesel fuel constituents, resulting from low-temperature or short-distance stop-start operation, can be approximately estimated from measurements of the flash point of the oil (ASTM D-92, IP 36) that is appreciably lowered by small quantities of fuel. The presence of gasoline constituents can be measured by distillation (ASTM D-322, IP 23) or by infrared spectroscopy.

Fire-resistant lubricating oil is used widely in the coal mining industry. The use of such fluids also is expanding in the metal cutting and forming, lumber, steel, aluminum, and aircraft industries. A test is also available to evaluate the fire-resistant properties of lubricating oil under a variety of conditions (ASTM D-5306). Most tests involve dripping, spraying, or pouring the liquid into a flame or onto a hot surface of molten metal, but in this test the fluid is impregnated into ceramic fiber media and the linear flame propagation rate, used for the comparison of relative flammability is measured.

12.3.11. Oxidation Stability

Oxidation results in the development of acidic products that can lead to corrosion and can also affect the ability of the oil to separate from water.

Oxidation can also lead to an increase in viscosity and the formation of sludge that can restrict oil paths, thus impairing circulation of the oil and interfering with the function of governors and oil relays. Correctly formulated turbine oils have excellent resistance to oxidation and will function satisfactorily for long periods without changing the system charge. Oxidation stability can be assessed by various tests (ASTM D-943, IP 114, IP 157) that use copper as well as iron as catalysts in the presence of water to simulate metals present in service conditions.

Although systems are usually designed to avoid entrainment of air in the oil, it is not always possible to prevent this, and the formation of a stable foam increases the surface area of the oil that is exposed to small bubbles of air, thus assisting oxidation. Defoaming agents are usually incorporated in turbine oils to decrease their foaming tendency, and this can be measured (ASTM D-892, IP 146). Air release is also an important property, and a careful choice of type and amount of defoaming agents is necessary to provide the correct balance of foam protection and air release properties.

12.3.12. Pour Point

The pour point (ASTM D-97, IP 15) is the lowest temperature at which an oil will flow under specified test conditions, and it is roughly equivalent to the tendency of the oil to cease to flow from a gravity-fed system or from a container and is a guide to, but not an exact measure of, the temperature at which flow ceases under the service conditions of a specific system.

The pour point of wax-containing oils can be reduced by the use of special additives known as pour point depressants that inhibit the growth of wax crystals, thus preventing the formation of a solid structure. It is a recognized property of oil of this type that previous thermal history may affect the measured pour point. The test procedure (ASTM D-97, IP 15) also permits some measurement of the effect of thermal conditions on waxy oils.

The importance of the pour point to the user of lubricants is limited to applications where low temperatures are likely to influence oil flow. Obvious examples are refrigerator lubricants and automotive engine oils in cold climates. Any pump installed in outside locations where temperatures periodically fall below freezing should utilize lubricants with a pour point below those temperatures or the borderline pumping temperature can be determined by a designated test method (ASTM D-3829).

12.3.13. Thermal Stability

The panel coking test, when used in conjunction with other tests, can be used to assess the deposit-forming tendencies due to thermal instability, and

the available alkalinity of these oils can be measured (ASTM D-66, IP 177 IP 276).

12.3.14. Viscosity

The viscosity of lubricating oil is a measure of its flow characteristics. It is generally the most important controlling property for manufacture and for selection to meet a particular application. The viscosity of a mineral oil changes with temperature but not normally with high stress and shear rate (ASTM D-5275, ASTM D-5481, ASTM D-5684, IP 294), unless specific additives that may not be shear stable are included to modify the viscosity-temperature characteristics. Explosions can also result when lubricating oil is in contact with certain metals under high shear conditions (ASTM D-3115).

Thus for base oils, the rate of flow of the oil through a pipe or capillary tube is directly proportional to the pressure applied. This property is measured for most practical purposes by timing the flow of a fixed amount of oil through a calibrated glass capillary tube under gravitational force at a standard temperature and is known as the kinematic viscosity of the oil (ASTM D-445, IP 71). The unit of viscosity used in conjunction with this method is the centistoke (cSt), but this may be converted into the other viscosity systems (Saybolt, Redwood, Engler) by means of conversion formulae. At very high pressures, the viscosity of mineral oils increases considerably with increase in pressure, the extent depending on the crude source of the oil and on the molecular weight (ASTM D-2502, ASTM D-2878) of the constituent components.

Because the main objective of lubrication is to provide a film between load-bearing surfaces, the selection of the correct viscosity for the oil is aimed at a balance between a viscosity high enough to prevent the lubricated surfaces from contacting and low enough to minimize energy losses through excessive heat generation caused by having too viscous a lubricant (ASTM D-2422, BS-4231).

The standard viscosity temperature charts (ASTM D-341) are useful for estimating viscosity at the various temperatures that are likely to be encountered in service.

The viscosity of automotive engine oil is the main controlling property for manufacture and for selection to meet the particular service condition using the American Society of Automotive Engineers (SAE) viscosity classification. The higher-viscosity oils are standardized at 210°F (99°C), and the lighter oils that are intended for use in cold weather conditions are standardized at 0°F (–18°C).

The principal difference between the requirements of gas and other internal combustion engine oils is the necessity to withstand the degradation that can occur from accumulation of oxides of nitrogen in the oil that

are formed by combustion. The condition of gas engine oils in large engines can be followed by measuring oil viscosity increase (ASTM D-66, ASTM D-97, IP 177, IP 139) to determine changes in the neutralization value resulting from oxidation. In addition, analytical techniques such as infrared spectroscopy and membrane filtration can be used to check for nitration of the oil and buildup of suspended carbonaceous material.

The viscosity index is an empirical number that indicates the effect of change of temperature on the viscosity of an oil.

Multigrade motor oils do not behave as Newtonian oils, and the improved viscosity-temperature characteristics of multigrade oils enables, for example, an oil to be formulated to have mixed characteristics (ASTM D-2602, ASTM D-3829).

The viscosity index is important in applications in which an appreciable change in temperature of the lubricating oil could affect the operating characteristics of the equipment. Automatic transmissions for passenger vehicles are an example of this, where high-viscosity-index oils with improvers are used to minimize differences between a viscosity low enough to permit a sufficiently rapid gear shift when starting under cold conditions and a viscosity adequate at the higher temperatures encountered in normal running.

Paraffinic oils have the lowest rate of change of viscosity with temperature (highest viscosity index), whereas the naphthenic/aromatic oils have the highest rate of change (lowest viscosity index) (ASTM D-567, ASTM D-2270, IP 73, IP 226).

The viscosity index of multigrade automotive engine oils is typically in the range of 130–190, whereas monograde oils are usually between 85 and 105. The improved viscosity-temperature characteristics of multigrade oils enables, for example, an SAE 20W/50 oil to be formulated that spans SAE 20W viscosity characteristics at low temperatures and SAE 40 to 50 characteristics at the working temperature.

However, multigrade oils do not behave as Newtonian fluids and this is primarily due to the presence of polymeric viscosity index improvers. The result is that the viscosity of multigrade oils is generally higher at –18°C (0°F) than is predicted by extrapolation from 38°C (100°F) and 99°C (210°F) data, the extent of the deviation varying with the type and amount of viscosity index improver used. To overcome this, the SAE classification is based on a measured viscosity at –18°C (0°F) using a laboratory test apparatus known as a cold cranking simulator (ASTM D-2602).

12.3.15. Volatility

The volatility of lubricating oil is not usually an issue for multitesting. Nevertheless, tests are available so that specification and purity checks can be made (ASTM D-5480).

A method that is used to determine pitch volatility (ASTM D-4893) might also be used, on occasion, to determine the nonvolatility of lubricating oil. In the method, an aluminum dish containing about 15 g of accurately weighed sample is introduced into the cavity of a metal block heated and maintained at 350°C (662°F). After 30 min, during which the volatiles are swept away from the surface of the sample by preheated nitrogen, the residual sample is taken out and allowed to cool down in the desiccator. Nonvolatility is determined by the sample weight remaining and is reported as percent w/w residue.

A test is also available for the determination of engine oil volatility at 371°C (700°F), which is actually a requirement in some lubricant specifications (ASTM D-6417). This test method can be used on lubricant products not within the scope of other test methods with simulated distillation methodologies (ASTM D-2887). Applicability of this test method is limited to samples with an initial boiling point higher than 126°C. This test method may be applied to both lubricant oil base stocks and finished lubricants containing additive packages.

In the test, a sample aliquot diluted with a viscosity-reducing solvent is introduced into the gas chromatographic system, which uses a nonpolar open tubular capillary gas chromatographic column for eluting the hydrocarbon components of the sample in the order of increasing boiling point. The column oven temperature is raised at a reproducible linear rate to effect separation of the hydrocarbons. Quantitation is achieved with a flame ionization detector. The sample retention times are compared with those of known hydrocarbon mixtures, and the cumulative corrected area of the sample determined to the 371°C (700°F) retention time is used to calculate the percentage of oil volatilized at 371°C (700°F).

12.3.16. Water and Sediment

Knowledge of the water content of petroleum products is important in refining, purchase and sale, and transfer of products and is useful in predicting the quality and performance characteristics of the products.

The Karl Fischer test method ASTM D-6304) can be applied to the direct determination of water in lubricating oil. In this method, the sample injection in the titration vessel can be done volumetrically or gravimetrically. The instrument automatically titrates the sample and displays the result at the end of the titration. Viscous samples can be analyzed by using 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.

Sediment in lubricating oil can lead to system malfunction in critical applications, and determination of the amount of sediment is a necessity. In

the test method (ASTM D-2273), a 100-ml sample of oil is mixed with 50 ml of ASTM precipitation naphtha and is heated in a water bath at 32–35°C (90–95°F) for 5 min. The centrifuge tube containing the heated mixture is centrifuged for 10 min at a rate of between 600 and 700 relative centrifuge force (rcf). After the mixture is decanted carefully, the procedure is repeated with another portion of naphtha and oil. The final reading of sediment is recorded. This test method is not applicable in cases in which precipitated oil-soluble components will appreciably contribute to the sediment yield.

Insoluble material may form in lubricating oil in oxidizing conditions, and a test method is available (ASTM D-4310) to evaluate the tendency of lubricating oil to corrode copper catalyst metal and to form sludge during oxidation in the presence of oxygen, water, and copper and iron metals at an elevated temperature. This test method is a modification of another test method (ASTM D-943) in which the oxidation stability of the same kind of oils is determined by following the acid number of the oil. In the test method (ASTM D-4310), an oil sample is contacted with oxygen in the presence of water and iron-copper catalyst at 95°C (203°F) for 100 h. The weight of the insoluble material is determined gravimetrically by filtration of the oxidation tube contents through a 5-μm-pore size filter disk. The total amount of copper in the oil, water, and sludge phases is also determined.

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CHAPTER

13

GREASE

13.1. INTRODUCTION

Grease is a solid to semisolid product that consists of a lubricating fluid that has been gelled with a thickening agent so that the lubricant can be retained more readily into the required area (ASTM D-4950) (Gruse and Stevens, 1960; Guthrie, 1967; Berkley, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Warne, 1998; Speight, 2000; Banaszewski and Blythe, 2000).

Grease is used to prolong the life and increase the efficiency of mechanical devices by reducing friction and wear (ASTM D-4170, ASTM D-5707), and there are specific performance requirements (ASTM D-3527, ASTM D-4170, ASTM D-4289, ASTM D-4290, ASTM D-4693). Generally, a fluid lubricant (such as lubricating oil) is difficult to retain at the point of application and must be replenished frequently. On the other hand, a thickened fluid lubricant (grease) is easier to retain at the point of application, and lubrication intervals can be extended.

Grease varies in texture from soft to hard and in color from light amber to dark brown and, in contrast to liquid lubricants, will stay in place in a bearing assembly with comparatively elementary mechanical seals. Grease also assists in sealing against extraneous material and will lubricate without constant replenishment.

13.2. PRODUCTION AND PROPERTIES

Grease is, essentially, a two-phase system comprised of a liquid-phase lubricant (the liquid phase) containing a uniformly dispersed, finely divided thickener (the solid phase).

The largest volume of grease in use is made from petroleum products produced from naphthenic, paraffinic, blended, hydrocracked, hydrogenated, and solvent-refined stocks. In addition to petroleum oils, other lubricating fluids, such as esters, diesters, silicones, polyethers, and synthetic hydrocarbons, are also used. Of the synthetic fluids used in grease manufacture, the most common type is poly(alpha)olefin (PAO).

Grease is lubricating oil to which a thickening agent has been added for the purpose of holding the oil to surfaces that must be lubricated. The most widely used thickening agents are soaps of various kinds, and grease manufacture is essentially the mixing of soaps with lubricating oils. Until a relatively short time ago, grease making was considered an art. To stir hot soap into hot oil is a simple business, but to do so in such a manner as to form a grease is much more difficult, and the early grease maker needed much experience to learn the essentials of the trade. Therefore, it is not surprising that grease making is still a complex operation. The signs that told the grease maker that the soap was *cooked* and that the batch of grease was ready to run have been replaced by scientific tests that follow the process of manufacture precisely.

The early grease makers made grease in batches in barrels or pans, and the batch method is still the chief method of making grease. Oil and soap are mixed in kettles that have double walls between which steam and water may be circulated to maintain the desired temperature. When temperatures higher than 150°C (300°F) are required, a kettle heated by a ring of gas burners is used. Mixing is usually accomplished in each kettle by horizontal paddles radiating from a central shaft.

The soaps used in grease making are usually made in the grease plant, usually in a grease making kettle. Soap is made by chemically combining a metal hydroxide with a fat or fatty acid. The most common metal hydroxides used for this purpose are calcium hydroxide, lye, lithium hydroxide, and barium hydroxide. Fats are chemical combinations of fatty acids and glycerin. If a metal hydroxide is reacted with a fat, a soap containing glycerin is formed. Frequently a fat is separated into its fatty acid and glycerin components, and only the fatty acid portion is used to make soap. Commonly used fats for grease making soaps are cottonseed oil, tallow, lard, and degras. Among the fatty acids used are stearic acid (from tallow), oleic acid (from cottonseed oil), and animal fatty acids (from lard).

To make grease the soap is dispersed in the oil as fibers of such a size that it may only be possible to detect them by microscopy. The fibers form a matrix for the oil, and the type, amount, size, shape, and distribution of the soap fibers dictate the consistency, texture, and bleeding characteristics, as well as the other properties of grease. Grease may contain from 50% to 30% soap, and although the fatty acid influences the properties of grease, the metal in the soap has the most important effect. For example, calcium soaps form smooth, buttery grease that is resistant to water but is limited in use to temperatures under about 95°C (200°F).

The soaps may be combined with any lubricating oil, from a light distillate to a heavy residual oil. The lubricating value of the grease is chiefly dependent on the quality and viscosity of the oil. In addition to soap and oil, grease may also contain various additives that are used to improve the

ability of the grease to stand up under extreme bearing pressures, to act as a rust preventive, and to reduce the tendency of oil to seep or bleed from a grease. Graphite, mica, talc, or fibrous material may be added to grease that is used to lubricate rough machinery to absorb the shock of impact; other chemicals can make a grease more resistant to oxidation or modify the structure of the grease.

The older, more common method of grease making is the batch method, but grease is also made by a continuous method. The process involves soap manufacture in a series (usually three) of retorts. Soap making ingredients are charged into one retort, and soap is made in the second retort. The third retort contains finished soap, which is pumped through a mixing device in which the soap and the oil are brought together and blended. The mixer continuously discharges finished grease into suitable containers.

There are a variety of different types of grease that are produced with specific functions in mind. Therefore, properties vary with the method of preparation as well as with the metal included in the grease.

Calcium grease is resistant to water; it has a smooth texture, its chief use is for plain bearings and low-speed rolling bearings, and it has a high roll stability (ASTM D-1831). The water content of calcium grease usually varies between 0.4% and l.0%, is present in the form of water of crystallization, and has a stabilizing effect. High temperatures cause a loss of water and a consequent weakening of soap structure, and therefore the use of this grease is limited to a maximum temperature of about 60°C (140°F). Other stabilizers and structure modifiers can now be used in place of or as well as water, and the water content no longer has its former importance, for example, in calcium hydroxystearate grease, some of which can be used up to 120°C (248°F).

Calcium soap grease is one of the earliest known greases and is water resistant and mechanically stable. Calcium soap grease usually has a low melting point (dropping point; typically ~95°C/200°F). Anhydrous calcium soaps (usually calcium 12-hydroxystearate) are somewhat more temperature resistant, having a dropping point of about 150°C (300°F). Anhydrous calcium grease finds the greatest usage (when made with low-viscosity base oil) in operations where a wide range of climatic conditions is essential.

Sodium (soda) soap grease is fibrous in structure and is resistant to moderately high temperature but not to water. Sodium soap grease has a high dropping point (~175°C/350°F) than calcium grease. However, it tends to emulsify in the presence of water but has inherent rust protection properties. This grease is used for rolling bearings at higher temperatures and speeds than normal conventional calcium soap grease. The sodium can be determined by flame photometry (ASTM D-3340).

Lithium soap grease is normally smooth in appearance but may exhibit a grain structure. This type of grease is resistant to water and to the highest

normal service temperatures and, because of the variety of types, is often used as multipurpose grease. Lithium grease offers both the water resistance of calcium soap grease and the high-temperature properties of sodium soap grease. Grease prepared with lithium 12-hydroxystearate has a dropping point of about 190°C (375°F). The lithium can be determined by flame photometry (ASTM D-3340).

Aluminum soap grease is translucent and can be produced with aluminum soaps made in situ. In the process, the preformed soap (usually aluminum distearate) is dissolved in hot oil in a mixing grease kettle, and the hot mixture is poured into pans to cool. The cooling rate affects the final consistency. The final product is a smooth, transparent grease with poor shear stability but excellent oxidation and water resistance. Aluminum soap grease is water resistant and adhesive but tends to have poor mechanical stability and so is not suitable for rolling bearings.

Mixed soap grease (e.g., the sodium/calcium soap grease.) is manufactured for uses that include high-speed rolling bearings. On the other hand, *complex soap grease* contains calcium, calcium/lead, or other metallic complexes with fatty acids and acetate, benzoate, or other salts. The complex soap grease has a high dropping point (≥260°C/≥500°F). In addition, complex soap grease has excellent antioxidation characteristics as well as high resistance to water and good mechanical stability properties.

Aluminum complex grease has excellent water wash-off and spray-off characteristics as well as high-temperature resistance and is widely used in steel mill applications and automotive components subject to these conditions. *Calcium complex grease* has inherent extreme pressure properties (ASTM D-2596, ASTM D-5706) and provides good friction and wear performance (ASTM D-4170). *Lithium complex grease* performance is generally like that of lithium 12-hydroxystearate grease except it has a dropping point approximately 50°C (90°F) higher. Lithium complex grease provides good low-temperature performance and excellent high-temperature life performance in tapered roller bearings.

Clay-thickened grease is often referred to as nonmelting grease because of its tendency to decompose before reaching the dropping point (~290°C/550°F). This type of grease is water resistant and can be susceptible to severe degradation from other contaminants such as brine. The performance is not often equivalent to that of the conventional calcium soap grease or sodium soap grease Low-temperature performance could be considered satisfactory, but clay grease is not normally compatible with other grease, and protocols are available using other property test methods (ASTM D-566, ASTM D-2265, ASTM D-1831, ASTM D-1742, ASTM D-3527, ASTM D-4290, ASTM D-4049, IP 132) by which this can be determined.

Examples of other grease include the nonsoap types with high water resistance and mechanical stability and some from selected organic compounds; these are now being further developed for multipurpose use. Treated clays or organic dyes of high temperature resistance along with synthetic heat-resisting fluids are used for extreme temperatures. Nonsoap grease often contains solid additives, such as graphite and molybdenum disulfide (MoS_2) and is used under conditions of heavy loading (ASTM D-2509, IP 326) or high temperature.

13.3. TEST METHODS

The standard tests used to determine the properties of petroleum and petroleum products are commonly applied to grease. Among these are aniline point (ASTM D-611), carbon residue (ASTM D-189, ASTM D-524, ASTM D-4530, IP 13, IP 14, IP 398), fire point (ASTM D-92), flash point (ASTM D-92), pour point (ASTM D-97), and viscosity (ASTM D-445). However, because of the complexity of grease formulations and the variety of uses, many other tests are also deemed necessary to estimate performance in service. Other tests not included in this chapter may be found elsewhere under the test methods for lubricating oil (Chapter 12). Some modification of the test method may be necessary because of the different character of grease vis-à-vis lubricating oil.

13.3.1. Acidity and Alkalinity

Grease may contain small amounts of free organic acids but should not contain strong acids. In some conventional lime base grease small amounts of free organic acids are intended as an aid to stability. Grease may also contain small amounts of free alkalinity.

Methods of analysis (ASTM D-128, IP 37) are available for the measurement of excessive acidity derived from oxidation. These methods cover conventional grease that consists essentially of petroleum oil and soap. Thus these test methods are applicable to many types but not all grease. The constituents covered by the test series are soap, unsaponifiable matter (base oil), water, free alkalinity, free fatty acid, fat, glycerin, and insoluble. A supplementary test method is also provided and is intended for application to grease that contains thickeners that are essentially insoluble in *n*-hexane and to grease that cannot be analyzed by conventional methods because of the presence of such constituents as nonpetroleum fluids or nonsoap-type thickeners, or both. These methods may not be applicable to grease analysis when lead, zinc, or aluminum soaps are present or in the presence of some additives such as sodium nitrite.

13.3.2. Anticorrosion Properties

Water resistance alone does not ensure that grease will protect bearings or other mechanisms against moisture corrosion. Methods for assessing rust prevention by grease have been described (ASTM D-1743, IP 220).

In the former method (ASTM D-1743), a tapered roller bearing is packed with grease and after a short running-in period is dipped and stored above distilled water. The bearing is then cleaned and examined for corrosion. In the latter method (IP 220), the grease is tested in a ball bearing under dynamic conditions. The bearing is run intermittently in the presence of distilled water and at the end of the test is rated for corrosion.

Grease should not be corrosive to metals with which it come in contact, neither should it develop corrosion tendencies with aging or oxidation. A polished copper strip (ASTM D-4048) (other metals can also be used) is immersed in the grease that is stored at a temperature relevant to the use of the grease (IP 112). The metal strip is examined for etching, pitting, or discoloration. Alternatively, the test may be accelerated by storage of the grease and copper strip in an oxygen bomb under pressure (ASTM D-1261).

13.3.3. Composition

The lubricating fluids that can be thickened to form grease vary widely in composition and properties (Chapter 12).

An analytical procedure (ASTM D-l28) is available for the separation of grease into its component parts and their measurement. Spectrographic methods, such as flame photometry (ASTM D-3340), may also be used to determine the metal present as soaps or the wear elements in used grease, in conjunction with separation techniques to measure and identify the various types of fats, lubricating fluids, or additives present. The simpler tests that are more likely to be quoted are ash content, acidity and alkalinity, water, and dirt content.

Minerals and inorganic salts are determined as ash by ignition (ASTM D-128, IP 5),and the data include the bulk of clay-type nonsoap thickeners. The method includes a rapid routine method and a procedure in which sulfuric acid is added to avoid loss of the more volatile oxides, and the result is reported as sulfated ash.

Microscopic methods are used in the examination of used grease for particles that are an indicator of wear and are likely to be increased by the presence of abrasive dirt in grease; foreign particles are counted and graded for size under the microscope (IP 134) or by the extent to which deleterious particles scratch plates of polished acrylic plastic (ASTM D-l404).

In this method (ASTM D-1404), the test material is placed between two clean, highly polished plates held rigidly and parallel to each other in metal holders. The assembly is pressed together by squeezing the grease into a thin layer between the plastic plates. Any solid particles in the grease larger than the distance of separation of the plates and harder than the plastic will become imbedded in the opposing plastic surfaces. The apparatus is so constructed that one of the plates can be rotated about 30° with respect to the other while the whole assembly is under pressure, thereby causing the imbedded particles to form characteristic arc-shaped scratches in one or both plates. The relative number of such solid particles is estimated by counting the total number of arc-shaped scratches on the two plates.

The test offers a rapid means for estimating the number of deleterious particles in grease. However, a particle that is abrasive to acrylic plastic may not be abrasive to steel or other bearing materials. Therefore, the results of this test do not imply performance in field service.

Some grease may contain traces of water (ASTM D95, IP 74), sulfur (ASTM D-129), or chlorine (ASTM D-808, ASTM D-1317). Lithium and sodium in grease can be determined with flame photometry (ASTM D-3340).

13.3.4. Dropping Point

The *dropping point* (sometimes incorrectly used synonymously with *melting point*) is the temperature at which grease passes from a semisolid to a liquid state. As the temperature is raised, grease softens to the extent that it loses its self-supporting characteristic, the structure collapses, and the grease flows under its own weight; in a standard cup under standard conditions, this is called the dropping point. The change in state from a semisolid state to a liquid state is typical of grease containing soaps of conventional types added as thickeners. These tests are useful in identifying the types of grease and for establishing and maintaining benchmarks for quality control.

The dropping point is useful (1) in establishing benchmarks for quality control, (2) as an aid in identifying the type of thickener used in a grease, and (3) as an indication of the maximum temperature to which a grease can be exposed without complete liquefaction or excessive oil separation.

These test methods do not give identical results, and the dropping point should be quoted in terms of the method used (ASTM D-566, ASTM D-2265, IP 31, IP 132). The tests consist of heating a sample of grease (contained in a cup suspended in a test tube) in an oil bath at a prescribed rate. The temperature at which the material falls from the hole in the bottom of the cup is averaged with the temperature of the oil bath and recorded as the dropping point.

One test method (ASTM D-566, IP 132) is not recommended for temperatures above 288°C. In those cases, the alternate test method (ASTM D-2265) should be used.

13.3.5. Flow Properties

Grease is non-Newtonian in behavior, and, unlike oils, an initial shear stress (yield value) must be applied before it will deform and commence to flow. It is this nonflowing characteristic that enables grease to offer certain advantages over lubricating oils and results in its extensive use for the lubrication of rolling bearings.

One test method (ASTM D-1092) uses a procedure in which the grease is forced through short steel capillary tubes and the apparent viscosity is calculated as though the grease was in fact a Newtonian fluid. The test can be carried out over a range of temperatures. It has been used as a low-temperature test of grease pumpability (ASTM D-3245) and leads to a procedure for giving empirical data on flow rates for handling grease in long line dispensing systems. The borderline pumping temperature test method as developed for engine oil (ASTM D-3829) may also be applied to grease, with suitable modification to accommodate the physical properties of grease.

The consistency of grease is a critical parameter that helps define its ability to perform under given operating conditions. Consistency, as measured by penetration, is affected by temperature, but the penetration test is not suitable for determining the minor, yet sometimes significant, changes in consistency as the grease approaches temperatures at which phase changes in the thickener occur. Penetration is basically a flow measurement; in addition, other flow measurements can be utilized to evaluate this property at other conditions.

One test method (ASTM D-3232) can be used to evaluate flow properties of lubricating grease under high-temperature, low-shear conditions. In this method, a grease sample is packed into an annular channel in an aluminum block that is then placed on a hot plate capable of attaining temperatures in excess of 315°C (600°F) at a heating rate of 5 ± 1°C (9 ± 2°F)/min. A special trident probe spindle, attached to a viscometer, is lowered into the grease sample, and the hot plate is turned on. Simultaneously, the spindle is rotated at a constant 20 rpm, and torque measurements are read from the viscometer every minute. Readings are continued until the reading drops below 0.5 on the viscometer scale or until the maximum sample temperature of interest is attained. With these data and an appropriate conversion equation, a plot of apparent viscosity versus temperature is prepared.

Parameters that are important to grease behavior and utility are related to flow properties under pressure (ASTM D-2509, ASTM D-2596, ASTM

D-5706, IP 326) in determining the load-bearing properties of grease (ASTM D-2509, IP 326) and the wear-preventive characteristics of grease (ASTM D-2266, ASTM D-3704, ASTM D-4170). The significance of these tests is that they provide methods that can be used to differentiate among grease with low, medium, or high levels of extreme-pressure properties.

13.3.6. Low-Temperature Torque

Grease becomes harder and more viscous as the temperature drops and in extreme cases can become so rigid that excessive torque occurs within the bearing and there is a need to determine the ability of grease facilitate to machine starting and lubricating ability at subzero temperatures.

Measurement of low-temperature torque (ASTM D-1478) requires that a pregreased ball bearing is cooled to the desired temperature and the starting and running torques are determined at 1 rpm. This test method covers the determination of the extent to which a grease retards the rotation of a slow-speed ball bearing by measuring starting and running torques at low temperatures lower than –20°C (lower than –4°F). In the test method, a No. 6204 open ball bearing is packed completely full of grease and cleaned off flush with the sides. The bearing remains stationary while ambient temperature is lowered to the test temperature and held there for 2 h. At the end of this time, the inner ring of the ball bearing is rotated at 0.05 r/min while the restraining force on the outer ring is measured. Torque is measured by multiplying the restraining force by the radius of the bearing housing. Both starting torque and torque after 60 min of rotation are determined.

For applications with greater loads or larger bearings, another test method (ASTM D-4693) can be used to predict the performance of grease in automotive wheel bearings operating at low temperatures. This test determines the extent to which grease retards the rotation of a tapered roller bearing assembly. In this test, a sample of test grease is stirred and worked and a specified amount is packed into the two test bearings. The test assembly is heated to mitigate the effects of grease history; it is then cooled at a specified rate to –40°C (–40°F). A drive mechanism rotates the spindle at 1 rpm, and the torque required to prevent rotation of the hub is determined 60 s after the start of rotation.

13.3.7. Mechanical Stability

The ability of a grease to withstand a large degree of mechanical working without changing its consistency unduly can be important during the initial clearing stages in a bearing or in certain applications, for example, in a

bearing assembly under vibrating conditions. The effects of mechanical instability can lead in some cases to the grease becoming fluid and losing its sealing properties. Leakage (ASTM D-1263) from the assembly and inadequate lubrication can then follow.

The test method used to evaluate the leakage tendencies of wheel bearing grease (ASTM D-1263) provides a screening device that permits differentiation between products having distinctly different leakage characteristics. In the test method, the grease is distributed in a modified front-wheel hub and spindle assembly. The hub is rotated at a speed of 660 ± 30 rpm for 6 h ± 5 min at a spindle temperature, which is raised to and then maintained at 105 ± 1.2°C (221 ± 2°F). Leakage of grease, oil, or both is measured, and the condition of the bearing surface is noted at the end of the test.

The tests most widely used to assess mechanical stability are the prolonged worked penetration test (ASTM D-217-IP 50) and the roll test (ASTM D-1831). In the former test, the grease is subjected to a large number of strokes (usually 100,000) in a motorized version of the worker pot used for the penetration test at room temperature. In the roll test a measured amount of grease is placed in a horizontally mounted drum in which a steel roller rotates. The drum is turned about its axis, thereby subjecting the grease to a milling action similar to that occurring in rolling bearings. In both tests the difference in penetration of the grease, before and after, is a measure of the grease breakdown.

13.3.8. Oil Separation

Grease will often separate oil during storage and, if too much oil separates, the grease could harden to the extent that lubrication performance will be affected. Oil will be released from a grease at varying rates depending on the gel structure, the nature and viscosity of the lubricating fluid, and the applied pressure and temperature.

There are standard test methods (ASTM D 1742, ASTM D-3336, ASTM D-3337, ASTM D-3527, ASTM D-4425, IP 121) for predicting the amount of oil liberated by grease when stored in containers. In both methods the grease is supported by a wire mesh screen; a weight or air pressure is applied to the top surface of the grease to accelerate oil separation.

One particular method (ASTM D 1742, IP 121) is used to determine the tendency of lubricating grease to separate oil when stored at 25°C (77°F) at an applied air pressure of 1.72 kN/m^2 (0.25 psi). The test gives an indication of the oil retention characteristics of lubricating grease stored in both normally filled and partially filled containers. The duration of this test is either 24 h (ASTM D-1742) or 7 days (IP 121), and the data often correlate directly with oil separation that occurs in 16-kg (35 lb) containers of grease stored at room temperature.

Another test method (ASTM D-3336) is used to evaluate the performance characteristics of lubricating grease in ball bearings operating under light loads at high speeds and elevated temperatures for extended periods. Correlation with actual field service cannot be assumed. In this test, the lubricating grease is evaluated in a heat-resistant steel ball bearing rotated at 10,000 rpm under light loads at a specified elevated temperature up to 370°C (700°F). The test is run on a specified operating cycle until lubrication failure or completion of a specified time. With superior grease, tests can last up to several thousand hours.

In another test (ASTM D-3337), which is not the equivalent of long-term service performance tests, the data can be used to predict relative grease life at high temperature in a reasonable test period. In this test the bearing is run at 12,000 rpm with specified axial load. Although a test temperature of 250°C (482°F) may be specified, the equipment is capable of testing up to 315°C (600°F) if high-temperature bearings are used.

Another test method (ASTM D-3527) is used for the evaluation of grease life in tapered roller wheel bearings in a model front wheel assembly run at 1000 rpm under a specified thrust load at 160°C (320°F) with a cycle of 20 h on and 4 h off (ASTM D-4290).

13.3.9. Oxidation Stability

The storage stability of grease when packed into bearings is assuming considerable importance as more prepacked sealed-for-life bearings are adopted in industry. In these bearings the grease acts as a protective until the bearings are put into operation. Under such conditions thin films of grease in contact with steel or steel and bronze are exposed to air and moisture that promote oxidation of the grease, the products of which can cause corrosion of the bearing surfaces.

In the test method used to evaluate storage properties under these conditions (ASTM D-942, IP 142), oxidation of a thin film of grease is accelerated by heating the grease at 99°C (210°F) in oxygen at a pressure of 110 psi. The amount of oxygen absorbed by the grease is recorded in terms of pressure drop over a period of 100 h and in some cases up to 500 h. Grease that shows high oxygen absorption becomes fluid, increases in acidity and is generally considered unsatisfactory for use.

The oxidation induction time can also be used as an indication of oxidation stability. No correlation has been determined between the results of this test and service performance. In the test (ASTM D-5483) , a small quantity of grease in a sample pan is placed in a test cell. The cell is heated to a specified temperature and then pressurized with oxygen and is held at a regulated temperature and pressure until an exothermic reaction occurs. The extrapolated onset time is measured and reported as the oxidation

induction time. This test method covers lubricating grease that is subjected to oxygen at 500 psi and temperatures between 155 and 210°C (311 and 410°F).

13.3.10. Penetration

The cone penetration tests (ASTM D-217, ASTM D-1403, IP 50, IP 167, IP 310) are standard tests for determining the penetration of grease, and they provide an indication of the consistency of grease.

One particular test method (ASTM D-217) consists of four procedures. For unworked penetration, the cone assembly of the penetrometer is allowed to drop freely into the grease sample at 25°C (77°F) in a worker cup for 5 s. For worked penetration, the sample at 25°C (77°F) in a worker cup is subjected to 60 double strokes by the grease worker. The penetration is determined immediately by releasing the cone assembly from the penetrometer and allowing the cone to drop freely into the grease for 5 s. For prolonged worked penetration, the procedure is the same as for worked penetration, except that additionally before cone penetration, the sample is subjected to a predetermined number of double strokes in the grease worker. For block penetration, a cube of grease is used and the test is followed as for unworked penetration. The depth of penetration, measured in tenths of a millimeter, is the penetration value. A firm grease will have a low penetration value and, conversely, a soft grease will have a high penetration values.

The penetration varies according to the amount of shearing to which the grease has been subjected. It may be measured on the grease as received in its original container (undisturbed penetration), after transfer with minimum disturbance to a standard container (unworked penetration), after a standard amount of shearing (worked penetration), after a prolonged period of shearing in a mechanical worker (prolonged work penetration), and as a firm sample (block penetration).

13.3.11. Thermal Stability

Thermal conditions have a profound influence on the properties and performance of grease. And any one or more of several phenomena can occur consecutively or, even more likely, simultaneously (ASTM D-3336, ASTM D-3337, ASTM D-3527). Generally, grease having the least evaporative losses (ASTM D-972, ASTM D-2595) will probably perform longer in high-temperature service.

For example, grease softens and flows easier with an increase in temperature (ASTM D-3232), but the rate of oxidation of the grease also increases (ASTM D-942, IP 142). In addition, evaporation of oil con-

stituents also increases (ASTM D-972, ASTM D-2595) and the thickener melts or loses its ability to retain oil (ASTM D-566, ASTM D-2595, IP 132).

In one test method (ASTM D-972), the evaporative losses from grease or oils at any temperature in the range of l00–150°C (210–300°F) are determined. A weighed sample of grease is placed in an evaporation cell in an oil bath at the desired test temperature. Heated air at a specified flow rate is passed over the sample surface for 22 h, after which the loss in sample mass is determined. Another method (ASTM D-2595) used to supplement the original method (ASTM D-972) was developed because of higher service temperature and can be used to determine the loss of volatile materials from a grease over a temperature range of 93–316°C (200–600°F). This test uses an aluminum block heater instead of an oil bath (ASTM D-972) to achieve higher temperatures and should not be used at temperatures in excess of the flash point of the base oil of the grease. Both tests can be used to compare evaporation losses of grease intended for similar service, but the test results may not be representative of volatilization that can occur in service.

13.3.12. Viscosity

Grease is a non-Newtonian material insofar as flow is not initiated until stress is applied.

The *apparent viscosity* of grease is measured in poises (ASTM D-1092) and, because the apparent viscosity varies with both temperature and shear rate, the temperature and shear rate must be reported along with the measured viscosity. In this test, a sample of grease is forced through a capillary tube by a floating piston actuated by a hydraulic system using a two-speed gear pump. From the predetermined flow rate and the force developed in the system, the apparent viscosity is calculated. A series of 8 capillaries and 2 pump speeds provide 16 shear rates for the determination of apparent viscosities. The results are expressed in a log-log graph of apparent viscosity as a function of shear rate at a constant temperature or apparent viscosity at a constant shear rate as a function of temperature.

Apparent viscosity also is used to provide an indication of the directional value of starting and running torques of grease-lubricated mechanisms. Specifications may include limiting values of apparent viscosity for grease to be used at low temperature.

13.3.13. Volatility

The effective life of grease, especially under high-temperature conditions, is dependent on such factors as oxidation, retentive properties, and evaporation of the base oil. Evaporation of the oil can result in the grease becoming stiffer and drier and can ultimately lead to bearing failure.

The volatility of grease can be determined by a method (ASTM D-972, IP 183) in which air is passed at a known flow rate over a weighed amount of grease in a standard cell that is immersed in an oil bath at a required temperature. Because air is used some oxidation of the grease will occur, but nevertheless a comparative rating for evaporation loss can be obtained by measuring the loss in weight of the grease sample.

13.3.14. Water Resistance

The resistance of a grease to water contamination is an important property because grease has to lubricate mechanisms where water will be present to a greater or lesser extent. The presence of water can cause changes in grease consistency, emulsification with water-soluble soap base grease, and reduction in mechanical stability. The effects of such changes can lead to grease being washed out of the mechanisms, resulting in inadequate lubrication and poor protection against rusting. Most grease classed as water resistant is able to take up large amounts of water without suffering the serious changes mentioned above. It does not, however, follow that grease with high water resistance will afford adequate protection against rusting unless rust preventives are incorporated in the grease.

The most commonly used test for measuring water resistance is the water washout test method (ASTM D-1264, IP 215) in which a greased ball bearing is rotated at 600 rpm in an assembly with specified clearances in the covers to allow entry of water from a water jet that impinges on the face of one cover. The loss in grease pack after 1 h of operation is a measure of the resistance to water. The test serves only as a relative measure of the resistance of a grease to water washout.

Another test method (ASTM D 4049) is used to evaluate the ability of a grease to adhere to a metal panel when subjected to direct water spray. Test results correlate directly with operations involving direct water impingement. In this test, a 0.79-mm film of test grease is uniformly coated onto a stainless steel panel; then water, at 38°C (100°F), is sprayed directly on the panel for 5 min. The spray is controlled by specified spray nozzle, pump, and plumbing. After the spraying period, the panel is dried and weighed and the percentage of grease spray off is determined.

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CHAPTER

14

WAX

14.1. INTRODUCTION

Paraffin (petroleum) wax consists of the solid hydrocarbon residues remaining at the end of the refining process either in the lube stream (as mainly paraffin and intermediate waxes) or in the residual lube stock *tank bottoms* (as higher-melting microcrystalline waxes) (Gruse and Stevens, 1960; Guthrie, 1967; Gottshall and McCue, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Speight, 1999; Richter, 2000).

The waxy oil is fractionated to produce an oily wax called *slack wax*. This is separated by solvent extraction and fractionated into different melting point ranges to give waxes with a variety of physical characteristics. Paraffin waxes consist mainly of straight-chain alkanes (also called normal alkanes), with small amounts (3–15%) of branched-chain alkanes (or *iso*-alkanes), cycloalkanes, and aromatics. Microcrystalline waxes contain high levels of branched-chain alkanes (up to 50%) and cycloalkanes, particularly in the upper end of the molecular weight distribution. Paraffin waxes contain alkanes up to a molecular mass of approximately 600 amu, whereas microcrystalline waxes can contain alkanes up to a molecular mass of approximately 1100 amu.

During the refining of waxy crude oils, the wax becomes concentrated in the higher-boiling fractions used primarily for making lubricating oils. Refining of lubricating oil fractions to obtain a desirable low pour point usually requires the removal of most of the waxy components. The dewaxing step is generally performed by the chilling and filter pressing method, by centrifuge dewaxing, or by filtering a chilled solution of waxy lubricating oil in a specific solvent.

Wax provides improved strength, moisture proofing, appearance, and low cost for the food packaging industry, the largest consumer of waxes today. The coating of corrugated board with hot melts is of increasing importance to the wax industry. Other uses include the coating of fruit and cheese, the lining of cans and barrels, and the manufacture of anticorrosives. Because of its thermoplastic nature, wax lends itself to modeling and the making of replicas; blends of waxes are used by dentists when making dentures and

by engineers when mass-producing precision castings such as those used for gas turbine blades. The high gloss characteristic of some petroleum waxes makes them suitable ingredients for polishes, particularly for the "paste" type that is commonly used on floors, furniture, cars, and footwear. The highly refined waxes have excellent electrical properties and so find application in the insulation of low-voltage cables, small transformers, coils, capacitors, and similar electronic components.

14.2. PRODUCTION AND PROPERTIES

Paraffin wax from a solvent dewaxing operation (Speight, 1999) is commonly known as *slack wax*, and the processes used for the production of waxes are aimed at de-oiling the slack wax (petroleum wax concentrate).

Wax sweating was originally used to separate wax fractions with various melting points from the wax obtained from shale oils. Wax sweating is still used to some extent but is being replaced by the more convenient crystallization process. In wax sweating, a cake of slack wax is slowly warmed to a temperature at which the oil in the wax and the lower-melting waxes become fluid and drip (or sweat) from the bottom of the cake, leaving a residue of higher-melting wax. Sweated waxes generally contain small amounts of unsaturated aromatic and sulfur compounds, which are the source of unwanted color, odor, and taste that reduce the ability of the wax to resist oxidation; the commonly used method of removing these impurities is clay treatment of the molten wax.

Wax crystallization, like wax sweating, separates slack wax into fractions, but instead of using the differences in melting points, it makes use of the different solubility of the wax fractions in a solvent, such as the ketone used in the dewaxing process (Speight, 1999, Chapter 19). When a mixture of ketone and slack wax is heated, the slack wax usually dissolves completely, and if the solution is cooled slowly, a temperature is reached at which a crop of wax crystals is formed. These crystals will all be of the same melting point, and if they are removed by filtration, a wax fraction with a specific melting point is obtained. If the clear filtrate is further cooled, a second crop of wax crystals with a lower melting point is obtained. Thus by alternate cooling and filtration the slack wax can be subdivided into a large number of wax fractions, each with different melting points.

Chemically, paraffin wax is a mixture of saturated aliphatic hydrocarbons (with the general formula C_nH_{2n+2}). Wax is the residue extracted when lubricant oils are dewaxed and it has a crystalline structure with a carbon number greater than 12. The main characteristics of wax are (1) absence of color, (2) absence of odor, (3) translucence, and (4) a melting point above 45°C (113°F).

Petroleum wax is of two general types, the paraffin waxes in petroleum distillates and the microcrystalline waxes in petroleum residua. The melting

point of wax is not directly related to its boiling point, because waxes contain hydrocarbons of different chemical nature. Nevertheless, waxes are graded according to their melting point (ASTM D-87, IP 55) and oil content (ASTM D-721, IP 158).

A scheme for classifying waxes as either paraffin, semi-microcrystalline, or microcrystalline is based on the equation

$$n^2D = 0.000194\ 3t + 1.3994$$

where t is the congealing point temperature in °F (ASTM D-938, IP 76). Viscosity is included as an additional parameter.

Semi-microcrystalline wax and microcrystalline wax are petroleum waxes containing substantial portions of hydrocarbons other than normal alkanes. They are characterized by refractive indexes greater than those given by the above equation and by viscosities at 210°F of less than 10 cSt for semi-microcrystalline waxes or greater than 10 cSt for microcrystalline waxes. Microcrystalline waxes have higher molecular weights, smaller crystal structures, and greater affinities for oil than paraffin waxes. Microcrystalline waxes usually melt between 66°C (150°F) and 104°C (220°F) and have viscosities between 10 and 20 cSt at 99°C (210°F).

Petrolatum is usually a soft product containing approximately 20% oil and melting between 38°C (100°F) and 60°C (140°F). Petrolatum or petroleum jelly is essentially a mixture of microcrystalline wax and oil. It is produced as an intermediate product in the refining of microcrystalline wax or compounded by blending appropriate waxy products and oils. Petrolatum colors range from the almost black crude form to the highly refined yellow and white pharmaceutical grades.

The melting point of paraffin wax (ASTM D-87, IP 55) has both direct and indirect significance in most wax utilization. All wax grades are commercially indicated in a range of melting temperatures rather than at a single value, and a range of 1°C (2°F) usually indicates a good degree of refinement. Other common physical properties that help to illustrate the degree of refinement of the wax are color (ASTM D-156), oil content (ASTM D-721, IP 158), and viscosity (ASTM D-88, ASTM D-445, IP 71).

14.3. TEST METHODS

14.3.1. Appearance

Waxed coatings provide protection for packaged goods, and the high gloss characteristics provide improved appearance. Both the nature of the wax and the coating process contribute to the final gloss characteristics.

Specular gloss (ASTM D-1834) is the capacity of a surface to simulate a mirror in its ability to reflect an incident light beam. The glossimeter used to measure gloss consists of a lamp and lens set to focus an incident light beam 20° from a line drawn perpendicular to the specimen. A receptor lens and photocell are centered on the angle of reflectance, also 20° from a line perpendicular to the specimen. A black, polished glass surface with a refractive index of 1.54 is used for instrument standardization at 100 gloss units. A wax-coated paper is held by a vacuum plate over the sample opening. The light beam is reflected from the sample surface into the photocell and measured with a null-point microammeter.

The gloss is measured before (ASTM D-1834) and after (ASTM D-2895) aging the sample for 1 and 7 days in an oven at 40°C (104°F). The specified aging conditions are intended to correlate with the conditions likely to occur in the handling and storage of waxed paper and paperboard.

14.3.2. Barrier Properties

The ability of wax to prevent the transfer of moisture vapor is of primary concern in the food packaging industry. To maintain the freshness of dry foods, moisture must be kept out of the product, but to maintain the quality of frozen foods and baked goods the moisture must be kept in the product. This results in two criteria for barrier properties: moisture vapor transmission rates (A) at elevated temperatures and high relative humidity and (B) at low temperatures and low relative humidity, for frozen foods.

The wax *blocking point* is the lowest temperature at which film disruption occurs across 50% of the waxed paper surface when the test strips are separated. The *picking point* is the lowest temperature at which the surface film shows disruption. Blocking of waxed paper, because of the relatively low temperature at which it may occur, can be a major problem for the paper coating industry. The wax picking and blocking points indicate an approximate temperature range at or above which waxed surfaces in contact with each other are likely to cause surface film injury.

To determine the blocking point of wax (ASTM D-2618, ASTM D-1465), two paper test specimens are coated with the wax sample, folded with the waxed surfaces together, and placed on a blocking plate that is heated at one end and cooled at the other to impose a measured temperature gradient along its length. After a conditioning period on the plate, the specimens are removed, unfolded, and examined for film disruption. The temperatures of corresponding points on the blocking plate are reported as the picking and blocking points or as the blocking range.

The *sealing strength* of petroleum wax is determined in a test (ASTM D2005) in which two paper specimens, 5×10 in., are cut and sealed together by passing them over a heated bar. The sealed papers are conditioned at

73°F (23°C) and 50% relative humidity for 17–24 h. Test specimens, 10 × 15 cm, are cut from the sealed paper and delaminated at the rate of 5 in./min. The open ends of the seal are in the same plane, with a 180° angle between the ends. The unseparated portion is perpendicular to this plane. Sealing strength is the force measured in grams per centimeter required to separate the sealed strips.

14.3.3. Carbonizable Substances

Wax and petrolatum intended for certain pharmaceutical purposes are required to pass the test for carbonizable matter. The degree of unsaturation (carbonizable material) is determined by reacting the wax with concentrated sulfuric acid. The resultant color of the acid layer must be lighter than the reference color if the wax is to qualify as pharmaceutical grade. The melting point (ASTM D-87, IP 55) for such grades may also be required.

To determine the presence of carbonizable substances in paraffin wax (ASTM D-612) 5 ml of concentrated sulfuric acid is placed in a graduated test tube and 5 ml of the melted wax are added. The sample is heated for 10 min at 70°C (158°F). During the last 5 min the tube is shaken periodically. The acid layer is compared with a standard reference solution, and the wax sample passes if the color is not darker than the standard color.

14.3.4. Color

Paraffin wax is generally white in color, whereas microcrystalline wax and petrolatum range from white to almost black. A fully refined wax should be virtually colorless (*water-white*) when examined in the molten state. Absence of color is of particular importance in wax used for pharmaceutical purposes or for the manufacture of food wrappings. The significance of the color of microcrystalline wax and petrolatum depends on the use for which they are intended. In some applications (for example, the manufacture of corrosion preventives) color may be of little importance.

The Saybolt color test method (ASTM D-156) is used for nearly colorless waxes, and in this method a melted sample is placed in a heated vertical tube mounted alongside a second tube containing standard color disks. An optical viewer allows simultaneous viewing of both tubes. The level of the sample is decreased until its color is lighter than that of the standard and the color number above this level is the Saybolt color.

The test method for the color of petroleum products (ASTM D-1500, IP 196) is used for wax and petrolatum that are too dark for the Saybolt colorimeter. A liquid sample is placed in the test container, a glass cylinder of 30- to 35-mm ID, and compared with colored glass disks ranging in value

from 0.5 to 8.0 by using a standard light source. If an exact match is not found, and the sample color falls between two standard colors, the higher of the two colors is reported.

The Lovibond tintometer (IP 17) is used to measures the tint and depth of color by comparison with a series of red, yellow, and blue standard glasses. Waxes and petrolatum are tested in the molten state, and a wide range of cell sizes is available for the different types.

14.3.5. Composition

Almost all physical and functional properties of the wax are affected by:

1. The molecular weight range,
2. Distribution of its individual components, and
3. The degree of branching of the carbon skeleton.

For a given melting point, a narrow-cut wax consisting almost entirely of straight-chain paraffins will be harder and more brittle and will have a higher gloss and blocking point than a wax of broader cut or one containing a higher proportion of branched molecules.

All petroleum-derived waxes, including blends of waxes, from n-C_{17} to n-C_{44} can be separated by capillary column chromatography (ASTM D-5442). In this method, the sample is diluted in a suitable solvent with an internal standard, after which it is injected into a capillary column meeting a specified resolution, and the components are detected with a flame ionization detector. The eluted components are identified by comparison with a standard mixture, and the area of each straight-chain and branched-chain alkane is measured.

The polynuclear aromatic content of waxes can be estimated by the ultraviolet absorbance (ASTM D-2008) of an extract of the sample. In this test method, the ultraviolet absorbance is determined by measuring the absorption spectrum of the undiluted liquid in a cell of known path length under specified conditions. The ultraviolet absorptivity is determined by measuring the absorbance, at specified wavelengths, of a solution of the liquid or solid at known concentration in a cell of known path length.

The composition of wax is available through alternate procedures that involve solvent extraction (ASTM D-721, ASTM D-3235, IP 158), and the refractive index (ASTM D-1747) can also give an indication of composition, but mainly purity.

The solvent-extractable constituents of a wax may have significant effects on several of its properties such as strength, hardness, flexibility, scuff resistance, coefficient of friction, coefficient of expansion, and melting point. In

the test method (ASTM D-3235), the sample is dissolved in a mixture of 50% v/v methyl ethyl ketone and 50% v/v toluene. The solution is cooled to –32°C (–25°F) to precipitate the wax and then filtered. The yield of solvent-extractable constituents is determined by evaporating the solvent from the filtrate and weighing the residue.

14.3.6. 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 a mass basis via density measurements. This property is almost synonymously termed 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.

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 a liquid at test temperatures between 15 and 35°C (59–95°F). This test method applies to petroleum oils with high vapor pressures provided that 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 (59–95°F) that have vapor pressures below 600 mmHg and viscosities below about 15,000 cSt at the temperature of 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.

14.3.7. Hardness

Hardness is a measure of resistance to deformation or damage; hence it is an important criterion for many wax applications. It is indirectly related to blocking tendency and gloss. Hard, narrow-cut waxes have higher blocking points and better gloss than waxes of the same average molecular weight but wider molecular weight range.

The measurement of the needle penetration of petroleum wax (ASTM D1321, IP 376) gives an indication of the hardness or consistency of wax. This method uses a penetrometer applying a load of 100 g for 5 s to a standard needle with a truncated cone tip. The sample is heated to 17°C (30°F) above its congealing point, poured into a small brass cylinder, cooled, and placed in a water bath at the test temperature for 1 h. The sample is then positioned under the penetrometer needle, which when released penetrates into the sample. The depth of penetration in tenths of millimeters is reported as the test value. This method is not applicable to oily materials or petrolatum, which have penetrations greater than 250.

The method for the determination of the cone penetration of petrolatum (ASTM D937, IP 179) is used for soft wax and petrolatum. It is similar to the method for determining the needle penetration (ASTM D-132l) except that a much larger sample mould is used and a cone replaces the needle. The method requires that a 150-g load be applied for 5 s at the desired temperature.

14.3.8. Melting Point

The *melting point* is one of the most widely used tests to determine the quality and type of wax because wax is, more often than not, sold on the basis of the melting point range (ASTM D-87, ASTM D-4419, IP 55).

Table 14.1. Melting Point of Pure *n*-Hydrocarbons

Number of C Atoms	Melting Point °C	Number of C Atoms	Melting Point °C
1	–182	20	36
2	–183	21	40
3	–188	22	44
4	–138	23	47
5	–130	24	51
6	–95	25	54
7	–91	26	56
8	–57	27	59
9	–54	28	61
10	–30	29	64
11	–26	30	66
12	–10	31	68
13	–5	32	70
14	6	33	71
15	10	34	73
16	18	35	75
17	22	40	82
18	28	50	92
19	32	60	99

Petroleum wax, unlike the individual hydrocarbons (Table 14.1) does not melt at sharply defined temperatures because it is a mixture of hydrocarbons with different melting points but usually has a narrow melting range. Thus measurement of the melting point (more correctly, the *melting range*) may also be used as a means of *fingerprinting* wax to obtain more precise quality control and detailed information. Microcrystalline waxes and petrolatum are more complex and therefore melt over a much wider temperature range.

In the method (ASTM D-87, IP 55), a molten wax specimen is placed in a test tube fitted with a thermometer and placed in an air bath, which in turn is surrounded by a water bath held at 16–28°C (60–80°F). As the molten wax cools, periodic readings of its temperature are taken. When solidification of the wax occurs, the rate of temperature change decreases, yielding a plateau in the cooling curve. The temperature at that point is recorded as the melting point (cooling curve) of the sample. This procedure is not suitable for microcrystalline wax, petrolatum, or waxes containing large amounts of nonnormal hydrocarbons (the plateau rarely occurs in cooling curves of such waxes).

The method of determining the *drop melting point of* petroleum wax, including petrolatum (ASTM D127, IP 133) can be used for most petro-

leum waxes and wax-resin blends. In this method, samples are deposited on two thermometer bulbs by dipping chilled thermometers into the sample. The thermometers are then placed in test tubes and heated in a water bath until the specimens melt and the first drop falls from each thermometer bulb. The average of the temperatures at which these drops fall is the drop melting point of the sample.

The *congealing point* of petroleum wax, including petrolatum (ASTM D-93, IP 76), is determined by dipping a thermometer bulb in the melted wax and placing it in a heated vial. The thermometer is held horizontally and slowly rotated on its axis. As long as the wax remains liquid, it will hang from the bulb as a pendant drop. The temperature at which the drop rotates with the thermometer is the congealing point. The congealing point of microcrystalline wax or petrolatum is invariably lower than its corresponding drop melting point.

On the other hand, the *solidification point of* wax is the temperature in the cooling curve of the wax where the slope of the curve first changes significantly as the wax sample changes from a liquid to a solid state. In the test method (ASTM D-3944), a sample of wax is placed in a test tube at ambient temperature and heated above the solidification point of the wax sample. A thermocouple probe, attached to a recorder, is inserted into the wax sample, which is allowed to cool to room temperature. The thermocouple response of the cooling wax traces a curve on the chart paper of the recorder. The first significant change in the slope of the curve is the softening point.

14.3.9. Molecular Weight

The molecular weight of various waxes may differ according to (1) the source of the wax (whether it originated in lighter- or heavier-grade lubricating oils) and (2) the processing of the wax (the closeness of the distillation cut or the fractionation by crystallization). Thus the average molecular weight of a wax may represent an average of a narrow or a wide band of distribution.

Generally, for any series of similar waxes, an increase in molecular weight increases viscosity and melting point. However, many of the other physical and functional properties are more related to the hydrocarbon types and distribution than to the average molecular weight.

In the test method for molecular weight (ASTM D-2503) a small sample of wax is dissolved in a suitable solvent, and a droplet of the wax solution is placed on a thermistor in a closed chamber in close proximity to a suspended drop of the pure solvent on a second thermistor. The difference in vapor pressure between the two positions results in solvent transport and condensation onto the wax solution, with a resultant change in tempera-

ture. Through suitable calibration, the observed effect can be expressed in terms of molecular weight of the wax specimen as a number average molecular weight.

14.3.10. Odor and Taste

The odor of wax is an important property in some uses of wax such as food packaging and is often included in the specifications of petroleum wax.

The odor of petroleum wax (ASTM D-1833, IP 185) is determined by a method in which 10 g of wax is shaved, placed in an odor-free glass bottle, and capped. After 15 min the sample is evaluated in an odor-free room by removing the cap and sniffing lightly. A rating of 0 (no odor) to 4 (very strong odor) is given by each member of a chosen panel. The reported value is the average of the individual ratings.

However, subjective evaluations such as odor and taste are difficult to standardize because even with a standardized method involving a group of experts there may be a difference of opinion as to what constitutes an acceptable odor or taste. A specific example is wine tasting.

14.3.11. Oil Content

The oil content of paraffin waxes is an indication of the degree of refinement, and fully refined wax usually has an oil content of less than 0.5%. Wax containing more than this amount of oil is referred to as *scale wax*, although an intermediate grade known as *semirefined wax* is sometimes recognized for wax having an oil content of about 1%.

Excess oil tends to exude from paraffin wax, giving it a dull appearance and a greasy feel. Such a wax would obviously be unsuitable for many applications, particularly the manufacture of food wrappings. A high oil content tends to plasticize the wax and has an adverse effect on sealing strength, tensile strength, hardness, odor, taste, color, and particularly color stability.

During wax refining increasing amounts of oil are removed, and this process must be controlled. Also, the oil content of slack waxes, petrolatum, and waxes must be assessed for end user specification. For high-oil-content waxes (i.e., greater than 15% w/w), the method (ASTM D-3235) involves dissolving a weighed amount of wax in a mixture of methyl ethyl ketone (MEK) and toluene, followed by cooling to –32°C (–27°F) to precipitate the wax. The oil and solvent are removed; then the solvent is evaporated off to produce a weighable amount of oil. Gas-liquid chromatographic (GLC) analysis of the solvent-extracted material has shown that the determined oil contains a small amount of additional wax, *n*-C_{17} to *n*-C_{22} alkanes, thereby producing a small error.

For wax containing less than 15% oil, the method (ASTM D-721, IP 158) is similar to that for high-oil-content waxes (ASTM D-3235) but uses only methyl ethyl ketone as the solvent. The concept that the oil is much more soluble than wax in methyl ethyl ketone at low temperatures is utilized in this procedure. A weighed sample of wax is dissolved in warm methyl ethyl ketone in a test tube and chilled to –32°C (–25°F) to precipitate the wax. The solvent-oil solution is separated from the wax by pressure filtration through a sintered glass filter stick. The solvent is evaporated, and the residue is weighed.

Microcrystalline waxes have a greater affinity for oil than paraffin waxes because of their smaller crystal structure. The permissible amount depends on the type of wax and its intended use.

The oil content of microcrystalline wax is, in general, much greater than that of paraffin wax and could be as high as 20%. Waxes containing more than 20% oil would usually be classed as petrolatum, but this line of demarcation is by no means precise.

14.3.12. Peroxide Content

The deterioration of petroleum wax results in the formation of peroxides and other oxygen-containing compounds. The test method for determination of the peroxide number measures those compounds that will oxidize potassium iodide. Thus the magnitude of the peroxide number is an indication of the quantity of oxidizing constituents present. In the test method (ASTM D-1832), a sample is dissolved in carbon tetrachloride and is acidified with acetic acid. A solution of potassium iodide is added, and after a reaction period, the solution is titrated with sodium thiosulfate and a starch indicator.

Suitable antioxidants, such as 2,6-di-tertiary butyl-*p*-cresol and butylated hydroxyanisole, may be added to the wax to retard the oxidation reactions.

14.3.13. Slip Properties

Friction is an indication of the resistance to sliding exhibited by two surfaces in contact with one another. The intended application determines the degree of slip desired. Coatings for packages that require stacking should have a high coefficient of friction to prevent slippage in the stacks. Folding box coatings should have a low coefficient of friction to allow the boxes to slide easily from a stack of blanks being fed to the forming and filling equipment.

The coefficient of kinetic friction for wax coatings (ASTM D-2534) is determined by fastening a wax-coated paper to a horizontal plate attached

to the lower, movable cross arm of an electronic load cell-type tensile tester. A second paper is taped to a 180-g sled that is placed on the first sample. The sled is attached to the load cell by a nylon monofilament passing around a frictionless pulley. The kinematic coefficient of friction is calculated from the average force required to move the sled at 35 in./min divided by the sled weight.

In this same vein, the abrasion resistance of wax is also an important property and can be determined by a standard test method (ASTM D-3234).

14.3.14. Storage Stability

The presence of peroxides or similar oxy-compounds is usually the result of oxidation and deterioration of waxes either in use or storage. Antioxidants, such as butylated hydroxyanisole, may be used to retard oxidation.

The peroxide number of petroleum wax (ASTM D-1832) is determined by dissolving a sample in carbon tetrachloride, acidifying with acetic acid, and adding a solution of potassium iodide; any peroxides present will react with the potassium iodide to liberate iodine, which is then titrated with sodium thiosulfate.

14.3.15. Strength

Another popular test for wax is the tensile strength (ASTM D-1320), which is considered to be a useful guide in controlling the quality of the wax, although the actual significance of the results obtained is not clear.

The method for determining the tensile strength of paraffin wax (ASTM D-1320) is an empirical evaluation of the tensile strength of waxes that do not elongate more than 1/18th of an inch under the test conditions. Six dumbbell-shaped specimens, with a specified cross-sectional area are cast. The specimens are broken on a testing machine under a load that increases at the rate of 20 lb/s along the longitudinal axis of the sample. Values are reported as pounds per square inch.

To determine the modulus of rupture (breaking force in pounds per square inch) of petroleum wax (ASTM D-2004), a wax slab, $8 \times 4 \times 0.15$ in., is cast over hot water. Small strips, about 3×1 in., are cut from the center of the slab. The strips are placed lengthwise on the support beams of the apparatus, and a breaking beam is placed across the specimen parallel to the support beams. A steadily increasing load is applied by water delivered to a bucket suspended from the breaking beam. The modulus of rupture is calculated from an equation relating the thickness and width of the test specimen to the total weight required to break it.

14.3.16. Ultraviolet Absorptivity

For process control purposes, it may be desirable to monitor the total aromatic content of petroleum wax (ASTM D-2008).

The procedure tests the product as a whole, without including any separation or fractionation steps to concentrate the absorptive fractions. When wax or petrolatum is tested in this procedure, the specimen is dissolved in *iso*-octane, and the ultraviolet absorbance is measured at a specified wavelength such as 290 nm. The absorptivity is then calculated. This procedure, as such, is not a part of the federal specification.

Although this procedure shows good operator precision, interpretation of the results requires some caution. Because the test does not include any selective fractionation of the sample, it does not distinguish any particular aromatic. It is also subject to the errors arising from interferences or differences in strong or weak absorptivity shown by different aromatics. Therefore, the test is good for characterization but cannot be used for quantitative determination of aromatic content or any other absorptive component.

14.3.17. Viscosity

Viscosity of molten wax (ASTM D-3236) is of importance in applications involving coating or dipping processes because it influences the quality of coating obtained. Examples of such applications are paper converting, hot-dip anticorrosion coatings, and taper manufacturing.

Paraffin waxes do not differ much in viscosity, a typical viscosity being 3 ± 0.5 cSt at 99°C (210°F). Microcrystalline wax is considerably more viscous and varies over a wide range, 10–20 cSt at 99°C (210°F). Some hot melt viscosities exceed 20,000 cSt at 177°C (350°F).

Kinematic viscosity is measured by timing the flow of a fixed volume of material through a calibrated capillary at a selected temperature (ASTM D-445, IP 71). The unit of kinematic viscosity is the stokes, and kinematic viscosities of waxes are usually reported in centistokes. Saybolt Universal seconds can be derived from centistokes (ASTM D-2161):

$$\text{Saybolt seconds @ } 37.8°\text{C } (100°\text{F}) = \text{cSt} \times 4.635$$

$$\text{Saybolt seconds @ } 98.9°\text{C } (210°\text{F}) = \text{cSt} \times 4.667$$

Another method (ASTM D-2669) is suitable for blends of wax and additives with apparent viscosities up to 20,000 cP at 177°C (350°F). Apparent viscosity is the measurement of drag produced on a rotating spindle immersed in the test liquid. A suitable viscometer is equipped to use interchangeable spindles and adjustable rates of rotation. The wax blend is

heated by means of a heating mantle in an 800-ml beaker and continuously stirred until the test temperature is slightly exceeded. The sample is cooled to the test temperature, the stirring is discontinued, and the viscosity is measured. Viscosities over a range of temperatures are recorded and plotted on semilog paper to determine the apparent viscosity at any temperature in the particular region of interest.

14.3.18. Volatility

The boiling point distribution of paraffin wax provides an estimate of hydrocarbon molecular weight distribution that influences many of the physical and functional properties of petroleum wax. To a lesser extent, distillation characteristics also are influenced by the distribution of various molecular types; that is, *n*-paraffins, branched, or cyclic structures. In the case of the paraffin waxes that are predominantly straight chain, the distillation curve reflects the molecular size distribution.

In the most common distillation test (ASTM D-1160), fractions are obtained under reduced pressure such as 10 mm for paraffin waxes or at 1 mm for higher-molecular-weight waxes. The fractions are taken at intervals across the full distillable range, and the complete results may be reported. In some cases, and for brevity, the distillation results are reported as the temperature difference observed between the 5% off and 95% off cut points. Waxes having very a narrow width of cut will tend to be more crystalline and to have higher melting points, higher hardness and tensile strength properties, and less flexibility.

In the gas chromatographic method (ASTM D 2887), a sample of the test wax is dissolved in xylene and introduced into a gas chromatographic column that is programmed to separate the hydrocarbons in boiling point order by raising the temperature of the column at a reproducible, calibrated rate. When wax samples are used, the thermal conductivity detector is used to measure the amount of eluted fraction. The data obtained in this procedure are reported in terms of percentage recovered at certain fixed temperature intervals.

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CHAPTER

15

ASPHALT

15.1. INTRODUCTION

Asphalt is a dark brown to black cementitious material obtained from petroleum processing, which contains very high-molecular-weight molecular polar species called asphaltenes that are soluble in carbon disulfide, pyridine, aromatic hydrocarbons, and chlorinated hydrocarbons (Gruse and Stevens, 1960; Guthrie, 1967; Broome and Wadelin, 1973; Weissermel and Arpe, 1978; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Speight, 1992; Speight, 2000).

Asphalt derives its characteristics from the nature of its crude oil precursor, with some variation possible by choice of manufacturing process. Although there are a number of refineries or refinery units whose prime function is to produce asphalt, petroleum asphalt is primarily a product of integrated refinery operations (Fig. 15.1). Crude oil may be selected for these refineries for a variety of other product requirements, and the asphalt (or residuum) produced may vary somewhat in characteristics from one refinery-crude system to another.

The residua from which asphalt are produced were once considered the garbage of a refinery, have little value and little use other than as a road oil. In fact, delayed coking (once the so-called the refinery garbage can) was developed with the purpose of converting residua to liquids (valuable products) and coke (fuel). However, recognition that asphalt, a once-maligned product worth only $16 per ton, is now worth $150–$200 per ton has changed attitudes toward residua and asphalt. Detailed specifications are necessary for asphalt paving uses as well as for other uses of asphalt.

15.2. PRODUCTION AND PROPERTIES

Residua are the starting materials for asphalt, and therefore the properties of the asphalt depend on the properties of the residuum from which the asphalt is manufactured. Residua properties can vary, depending on the cut point of the residuum (Table 15.1).

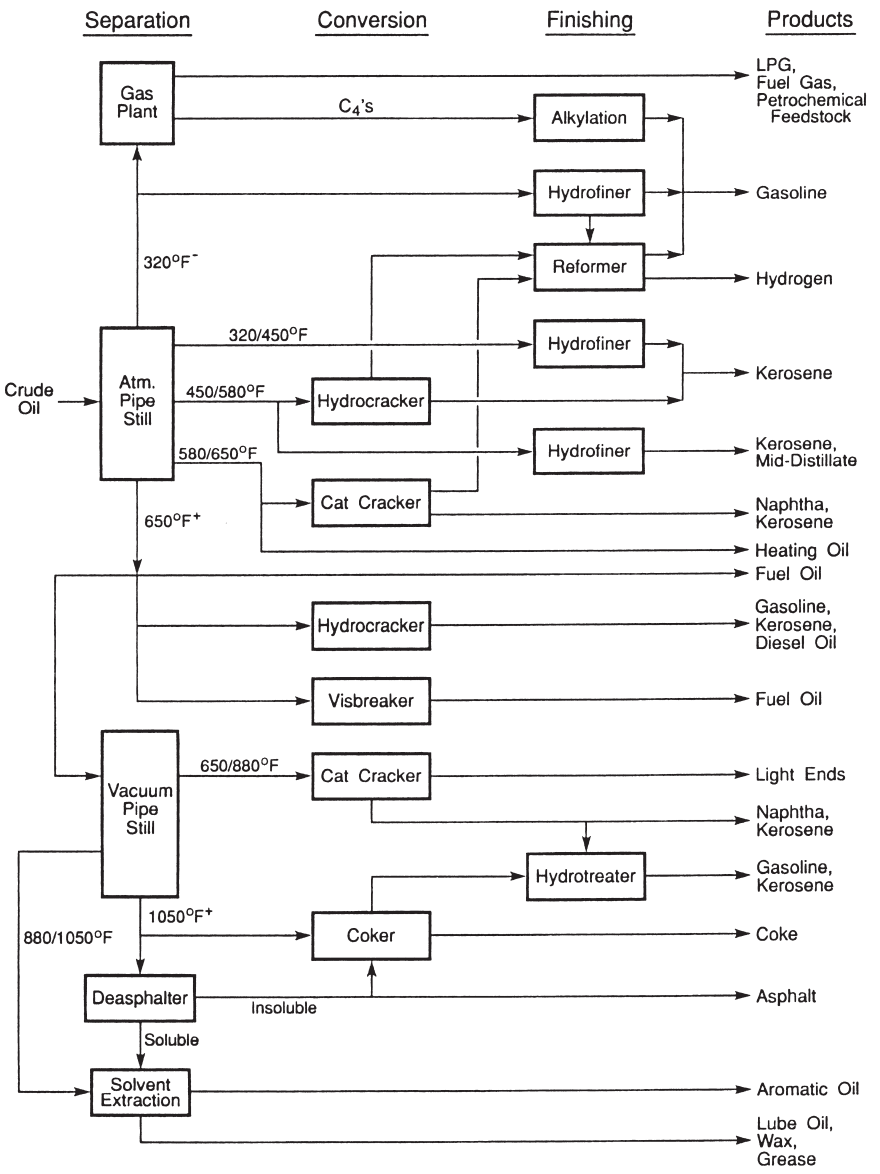

Figure 15.1. Schematic of a petroleum refinery (from Speight, 1999)

Table 15.1. Properties of Tia Juana Crude Oil and Different Residua (Adapted from Speight, 1999)

		Residua		
	Whole Crude	650°F+	950°F+	1050°F+
Yield, vol. %	100.0	48.9	23.8	17.9
Sulfur, wt. %	1.08	1.78	2.35	2.59
Nitrogen, wt. %		0.33	0.52	0.60
API gravity	31.6	17.3	9.9	7.1
Carbon residue, wt. %				
Conradson		9.3	17.2	21.6
Metals				
Vanadium, ppm		185		450
Nickel, ppm		25		64
Viscosity				
Kinematic				
At 100°F	10.2	890		
At 210°F		35	1010	7959
Furol				
At 122°F		172		
At 210°F			484	3760
Pour point, °F	–5	45	95	120

Asphalt manufacture involves distilling everything possible from crude petroleum until a residuum with the desired properties is obtained. This is usually done by stages (Fig. 15.2) in which distillation at atmospheric pressure removes the lower-boiling fractions and yields an atmospheric residuum (*reduced crude*) that may contain higher-boiling (lubricating) oils, wax, and asphalt. Distillation of the reduced crude under vacuum removes the oils (and wax) as overhead products, and the asphalt remains as a bottom (or residual) product. The majority of the polar functionalities and high-molecular-weight species in the original crude oil, which tend to be nonvolatile, concentrate in the vacuum residuum (Speight, 2000), thereby conferring desirable or undesirable properties on the asphalt.

At this stage the asphalt is frequently and incorrectly referred to as pitch and has a softening point (ASTM D-36, ASTM D-61, ASTM D-2319, ASTM D-3104, ASTM D-3461) related to the amount of oil removed and increasing with increasing overhead removal. In character with the elevation of the softening point, the pour point is also elevated (Table 15.1): The more oil distilled from the residue, the higher the softening point.

Asphalt is also produced by propane deasphalting (Fig. 15.3), and there are differences in the properties of asphalts prepared by propane deasphalting and those prepared by vacuum distillation from the same feed-

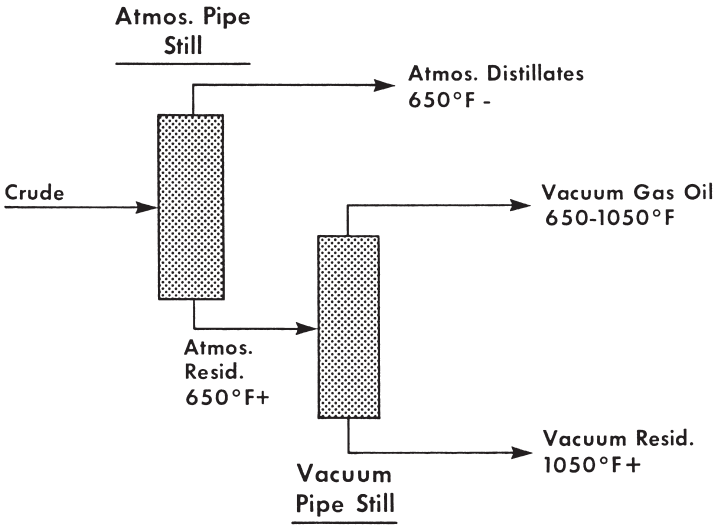

Figure 15.2. The distillation section of a refinery

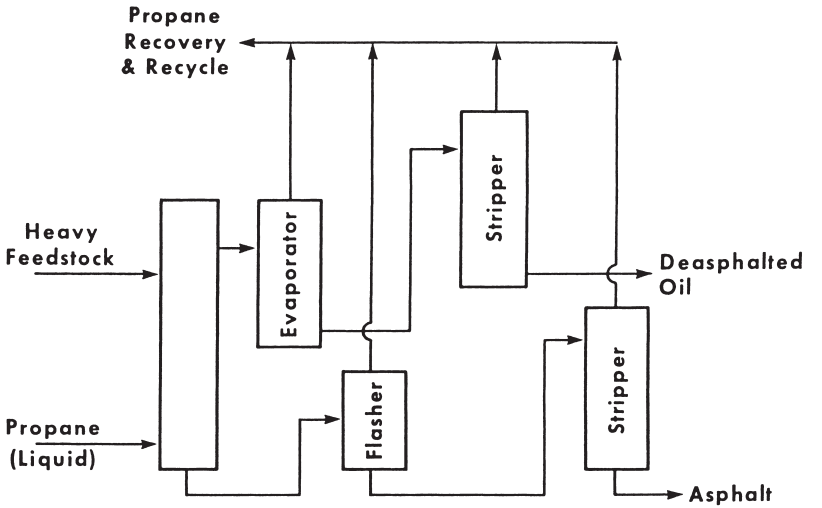

Figure 15.3. Propane deasphalting

stock. Propane deasphalting also has the ability to reduce a residuum even further and to produce an asphalt product with lower viscosity, higher ductility, and higher temperature susceptibility than other asphalts, although such properties might be anticipated to be very much crude oil dependent. Propane deasphalting is conventionally applied to low-asphalt-content

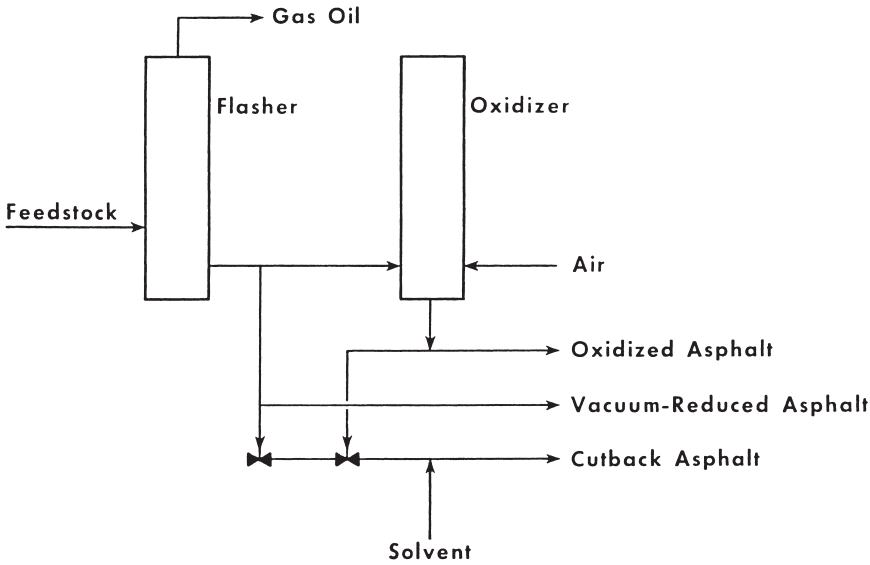

Figure 15.4. Asphalt manufacture including air blowing

crude oils, which are generally different in type and source from those processed by distillation of higher-yield crude oils. In addition, the properties of asphalt can be modified by air blowing in batch and continuous processes (Fig. 15.4) (Speight, 1992 and references cited therein; Speight, 2000 and references cited therein). On the other hand, the preparation of asphalts in liquid form by blending (cutting back) asphalt with a petroleum distillate fraction is customary and is generally accomplished in tanks equipped with coils for air agitation or with a mechanical stirrer or a vortex mixer.

An *asphalt emulsion* is a mixture of asphalt and an anionic agent such as the sodium or potassium salt of a fatty acid. The fatty acid is usually a mixture and may contain palmitic, stearic, linoleic, and abietic acids, and/or high-molecular-weight phenols. Sodium lignate is often added to alkaline emulsions to effect better emulsion stability. Nonionic cellulose derivatives are also used to increase the viscosity of the emulsion if needed. The acid number of asphalt is an indicator of its emulsifiability and reflects the presence of high-molecular-weight asphaltogenic or naphthenic acids. Diamines, frequently used as cationic agents, are made from the reaction of tallow acid amines with acrylonitrile, followed by hydrogenation. The properties of asphalt emulsions (ASTM D-977, ASTM D-2397) allow a variety of uses. As with other petroleum products, sampling is an important precursor to asphalt analysis and a standard method (ASTM D-140) is

available that provides guidance for the sampling of asphalts, liquid and semisolid, at point of manufacture, storage, or delivery.

15.3. TEST METHODS

The properties of asphalt are defined by a variety of standard tests that can be used to define quality (Table 15.2). Because the properties of residua vary with cut point (Table 15.1), the volume % of the crude oil helps the refiner produce asphalt of a specific type or property.

Specifications for paving asphalt cements usually include five grades differing in either viscosity or penetration level at 60°C (140°F) (ASTM D-496). Susceptibility of viscosity to temperature is usually controlled in asphalt cement by viscosity limits at a higher temperature such as 135°C (275°F) and a penetration or viscosity limit at a lower temperature such as 25°C (77°F). Paving cutbacks are also graded at 60°C (140°F) by viscosity, with usually four to five grades of each type. For asphalt cements, the newer viscosity grade designation is the midpoint of the viscosity range. The cutback's grade designation is the minimum kinematic viscosity for the grade, with a maximum grade viscosity of twice the minimum.

Roofing and industrial asphalts are also generally specified in various grades of hardness, usually with a combination of softening point (ASTM D-61, ASTM D-2319, ASTM D-3104, ASTM D-3461) and penetration to distinguish grades (ASTM D-312, ASTM D-449). Temperature susceptibility is usually controlled in these requirements by specifying penetration limits or ranges at 25°C (77°F) and other temperatures as well as softening point ranges at higher temperatures. Asphalt for built-up roof constructions are differentiated according to application depending primarily on pitch of the roof and to some extent on whether or not mineral surfacing aggregates are specified (ASTM D-312). The damp-proofing grades reflect above- or below-grade construction, primarily, and whether or not a self-healing property is incorporated.

The significance of a particular test is not always apparent from a reading of the procedure and sometimes can only be gained through working familiarity with the test. The following tests are commonly used to characterize asphalts, but these are not the only tests used for determining the property and behavior of an asphaltic binder. As in the petroleum industry, a variety of tests are employed that have evolved through local, or company, use.

15.3.1. Acid Number

The acid number is a measure of the acidity of a product and is used as a guide in the quality control of asphalt properties. Because a variety of

Table 15.2. Selected Tests for Determining Asphalt Properties

Test	Organization/Number	Description
Adsorption	ASTM D-4469	Calculation of degree of adsorption of an asphalt by an aggregate.
Bond and adhesion	ASTM D-1191	Used primarily to determine whether an asphalt has bonding strength at low temperatures. See also ASTM D-3141 and ASTM D-5078.
Breaking point	IP 80	Indication of the temperature at which an asphalt possesses little or no ductility and would show brittle fracture conditions.
Compatibility	ASTM D-1370	Indicates whether asphalts are likely to be incompatible and disbond under stress. See also ASTM D-3407.
Distillation	ASTM D-402	Determination of volatiles content; applicable to road oils and cutback asphalts.
Ductility	ASTM D-113	Expressed as the distance in cm which a standard briquet can be elongated before breaking; reflects cohesion and shear susceptibility.
Emulsified asphalts	ASTM D-244	Covers various tests for the composition, handling, nature and classification, storage, use, and specifications. See also ASTM D-977 and ASTM D-1187.
Flash point	ASTM D-92	Cleveland open cup method is commonly used; Tag open cup (ASTM D-3143) applicable to cutback asphalts.
Float test	ASTM D-139	Normally used for asphalts that are too soft for the penetration test.
Penetration	ASTM D-5	The extent to which a needle penetrates asphalt under specified conditions of load, time, and temperature; units are mm/10 measured from 0 to 300. See also ASTM D-243.
Sampling	ASTM D-140	Provides guidance for the sampling of asphalts.
Softening point	ASTM D-36	Ring and ball method; the temperature at which an asphalt attains a particular degree of softness under specified conditions; used to classify asphalt grades. See also ASTM D-2389.

Table 15.2. *Continued*

Test	Organization/Number	Description
Solubility in carbon disulfide	ASTM D-4	Determination of the carbon amount of carboids and/ or carbenes and mineral matter; trichloroethylene and 1,1,1-trichloroethane have been used for this purpose. See also ASTM D-2042.
Specific gravity	ASTM D-70	See also ASTM D-3142.
Stain	ASTM D-1328	Measures the amount of stain on paper or other cellulosic materials.
Temperature-volume correction	ASTM D-1250	Allows the conversion of volumes of asphalts from one temperature to another. See also ASTM D-4311.
Thin film oven test	ASTM D-1754	Determines the hardening effect of heat and air on a film of asphalt. See also ASTM D-2872.
Viscosity	ASTM D-2170	A measure of resistance to flow. See also ASTM D-88 (now discontinued but a useful reference), ASTM D-1599, ASTM D-2171, ASTM D-2493, ASTM D-3205, ASTM D-3381, ASTM D-4402, and ASTM D-4957.
Water content	ASTM D-95	Determines the water content by distillation with a Dean and Stark receiver.
Weathering	ASTM D-529	Used for determining the relative weather resistance of asphalt. See also ASTM D-1669 and ASTM D-1670.

oxidation products contribute to the acid number and the organic acids vary widely in service properties, the test is not sufficiently accurate to predict the precise behavior of asphalt in service.

Asphalt contains a small amount of organic acids and saponifiable material that is largely determined by the percentage of naphthenic (cycloparaffinic) acids of higher molecular weight that are originally present in the crude oil. With increased hardness, asphalt from a particular crude oil normally decreases in acid number as more of the naphthenic acids are removed during the distillation process. Acidic constituents may also be present as additives or as degradation products formed during service, such as oxidation products (ASTM D-5770). The relative amount of these materials can be determined by titrating with bases. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also some-

times used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

In a manner akin to the *acid number*, the *base number* (often referred to as the *neutralization number*) is a measure of the basic constituents in the oil under the conditions of the test. The base number is used as a guide in the quality control of oil formulation and is also used as a measure of oil degradation in service. The *neutralization number*, expressed as the *base number*, is a measure of the amount of basic substance in the oil always under the conditions of the test. The neutralization number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service; however, any condemning limits must be empirically established.

The *saponification number* expresses the amount of base that will react with 1 g of the sample when heated in a specific manner. Because certain elements are sometimes added to asphalt and also consume alkali and acids, the results obtained indicate the effect of these extraneous materials in addition to the saponifiable material present. In the test method (ASTM D-94, IP 136), a known weight of the sample is dissolved in methyl ethyl ketone or a mixture of suitable solvents and the mixture is heated with a known amount of standard alcoholic potassium hydroxide for between 30 and 90 min at 80°C (176°F). The excess alkali is titrated with standard hydrochloric acid, and the saponification number is calculated.

15.3.2. Asphaltene Content

The asphaltene fraction (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, 2000; 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 asphal-

tene fraction and if the presence of the solvent is not compensated by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in a large excess, the yields of the asphaltene fraction will vary and will be erroneous (Speight, 2000).

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 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 precipitating 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.

In another test method (ASTM D-4055), pentane-insoluble materials above 0.8 μm in size can be determined. In the test method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer the particulates onto the filter, which is then dried and weighed to give the yield of pentane-insoluble materials.

Another test method (ASTM D-893) that was originally designed for the determination of pentane- and toluene-insoluble materials in used lubricating oils can also be applied to asphalt. However, the method may need modification by first adding a solvent (such as toluene) to the asphalt before adding pentane. The pentane-insoluble constituents can include oil-insoluble materials. The toluene-insoluble materials can come from external contamination and products from degradation of asphalt. A significant change in the pentane-insoluble constituents or toluene-insoluble constituents indicates a change in asphalt that could lead to performance problems.

Two test methods are used. Procedure A covers the determination of insoluble constituents without the use of coagulant in the pentane and provides an indication of the materials that can be readily separated from the asphalt-solvent mixture by centrifugation. Procedure B covers the determination of insoluble constituents in asphalt containing additives and uses a coagulant. In addition to the materials separated by using procedure A, this coagulation procedure separates some finely divided materials that may be suspended in the asphalt. The results obtained by procedures A and B should not be compared because they usually give different values. The same procedure should be applied when comparing results obtained periodically on an oil in use or when comparing results determined in different laboratories.

In procedure A, a sample is mixed with pentane and centrifuged. The asphalt solution is decanted, and the precipitate is washed twice with pentane, dried, and weighed. For toluene-insoluble constituents a separate sample of the asphalt is mixed with pentane and centrifuged. The precipitate is washed twice with pentane, once with toluene-alcohol solution, and once with toluene. The insoluble material is then dried and weighed. In procedure B, procedure A is followed except that instead of pentane, a pentane-coagulant solution is used.

15.3.3. Bonding and Adhesion

The adhesion of asphalt to the mineral aggregate is a fundamental property of road asphalt. Once the adhesion deteriorates, the surface becomes unstable and unusable. There is a test method (ASTM D-1191) designed for use on crack and joint sealers that is used primarily to determine whether a jointing material possesses an arbitrary amount of bonding strength at low temperatures where portland cement concrete is being used.

15.3.4. Breaking Point (Fraas)

Brittle asphalt causes pavement instability. One particular test method (IP 80) is an approximate indication of the temperature at which asphalt possesses no ductility and would reflect brittle fracture conditions.

15.3.5. Carbon Disulfide-Insoluble Constituents

The component of highest carbon content is the fraction termed *carboids,* which consists of species that are insoluble in carbon disulfide or in pyridine. The fraction that has been called *carbenes* contains molecular species that are soluble in carbon disulfide and soluble in pyridine but are insoluble in toluene (Fig. 15.5).

Asphalt is a hydrocarbonaceous material that is made of constituents (containing carbon, hydrogen, nitrogen, oxygen, and sulfur) that are completely soluble in carbon disulfide (ASTM D-4). Trichloroethylene and 1,1,1-trichloroethane have been used in recent years as solvents for the determination of asphalt solubility (ASTM D-2042).

The carbene and carboid fractions are generated by thermal degradation or by oxidative degradation and are not considered to be naturally occurring constituents of asphalt. The test method for determining the toluene-insoluble constituents of tar and pitch (ASTM D-4072, ASTM D-4312) can be used to determine the amount of carbenes and carboids in asphalt.

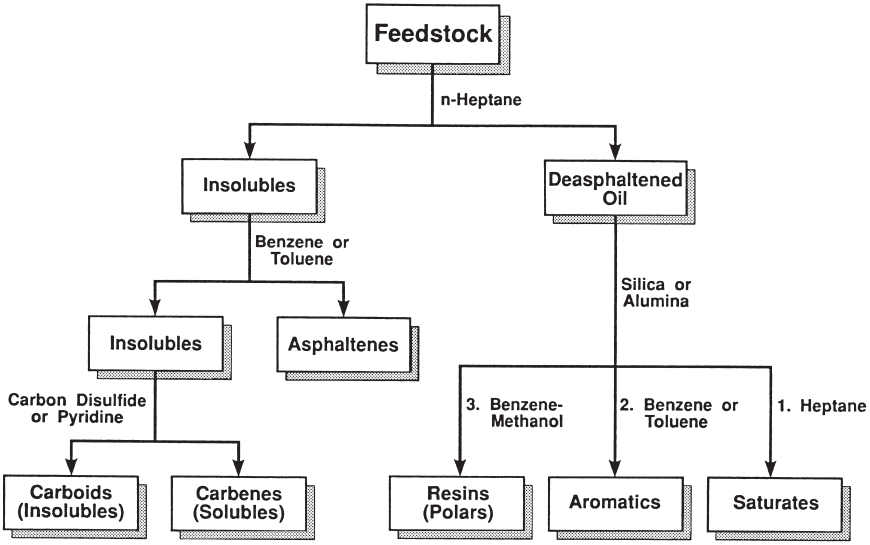

Figure 15.5. Feedstock fractionation

15.3.6. Carbon Residue

The *carbon residue* of asphalt serves as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat. The residue produced is also often used to provide thermal data that give an indication of the composition of the asphalt (Speight, 2000; Speight, 2001).

Tests for the Conradson carbon residue (ASTM D-189, IP 13), the Ramsbottom carbon residue (ASTM D-524, IP 14), the microcarbon carbon residue (ASTM D-4530, IP 398), and asphaltene content (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 dis-

tilled to a specified residue and the carbon residue test of choice then applied to the 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 D-524, 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 cracks 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 D-4530, IP 398) are equivalent to those produced by the Conradson carbon method (ASTM D-189, IP 13). However, the 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.

Other test methods that are used for determining the coking value of tar and pitch (ASTM D-2416, ASTM D-4715), which indicates the relative coke-forming properties of tars and pitches, might also be applied to asphalt. Both test methods are applicable to tar and pitch with an ash content ≤0.5% (ASTM D-2415). The former test method (ASTM D-2416) gives results close to those obtained by the Conradson carbon residue test (ASTM D-189, IP 13). However, in the latter test method (ASTM D-4715), a sample is heated for a specified time at 550 ± 10°C (1022 ± 18°F) in an electric furnace. The percentage of residue is reported as the coking value.

Finally, a method that is used to determine pitch volatility (ASTM D-4893) might also be used, on occasion, to determine the nonvolatility of asphalt. In the method, an aluminum dish containing about 15 g of accurately weighed sample is introduced into the cavity of a metal block heated and maintained at 350°C (662°F). After 30 min, during which any volatiles

are swept away from the surface of the sample by preheated nitrogen, the residual sample is taken out and allowed to cool down in the desiccator. Nonvolatility is determined by the sample weight remaining and reported as percentage w/w residue.

In any of the above 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.

15.3.7. Compatibility

When a coating asphalt and a saturating-grade asphalt are used together, as in prepared roofing, one test method (ASTM D-1370) indicates whether they are likely to bleed, show strike-through, or disbond under stress at the coating felt interface.

15.3.8. Composition

Determination of the composition of asphalt has always presented a challenge because of the complexity and high molecular weights of the molecular constituents. The principle behind composition studies is to evaluate asphalts in terms of composition and performance.

The methods used can be conveniently arranged into a number of categories: (a) fractionation by precipitation; (b) fractionation by distillation; (c) separation by chromatographic techniques; (d) chemical analysis by spectrophotometric techniques (infrared, ultraviolet, nuclear magnetic resource, X-ray fluorescence, emission, neutron activation), titrimetric and gravimetric techniques, and elemental analysis; and (e) molecular weight analysis by mass spectrometry, vapor pressure osmometry, and size exclusion chromatography.

However, fractional separation has been the basis for most asphalt composition analysis (Fig. 15.5). The separation methods that have been used divide asphalt into operationally defined fractions. Three types of asphalt separation procedures are now in use: (a) chemical precipitation in which *n*-pentane separation of asphaltenes is followed by chemical precipitation of other fractions with sulfuric acid of increasing concentration (ASTM D-2006); (b) adsorption chromatography with a clay-gel procedure in which, after removal of the asphaltenes, the remaining constituents are separated by selective adsorption/desorption on an adsorbent (ASTM D-2007 and ASTM D-4124); and (c) size exclusion chromatography in which gel permeation chromatographic (GPC) separation of asphalt constituents occurs based on their associated sizes in dilute solutions (ASTM D-3593).

The fractions obtained in these schemes are defined operationally or procedurally. The amount and type of asphaltenes in an asphalt are, for instance, defined by the solvent used for precipitating them. Fractional separation of asphalt does not provide well-defined chemical components. The materials separated should only be defined in terms of the particular test procedure (Fig. 15.5). However, these fractions are generated by thermal degradation or by oxidative degradation and are not considered to be naturally occurring constituents of asphalt. The test method for determining the toluene-insoluble constituents of tar and pitch (ASTM D-4072, ASTM D-4312) can be used to determine the amount of carbenes and carboids in asphalt.

In these methods, a sample is digested at 95°C (203°F) for 25 min and then extracted with hot toluene in an alundum thimble. The extraction time is 18 h (ASTM D-4072) or 3 h (ASTM D-4312). The insoluble matter is dried and weighed. Combustion will then show whether the material is truly carbonaceous or is inorganic ash from the metallic constituents (ASTM D-482, ASTM D-2415, ASTM D-4628, ASTM D-4927, ASTM D-5185, ASTM D-6443, IP 4).

Another method (ASTM D-893) covers the determination of pentane- and toluene-insoluble constituents in used lubricating oils and can be applied to asphalt. Pentane-insoluble constituents include oil-insoluble materials, and toluene-insoluble constituents can come from external contamination and highly carbonized materials from degradation. A significant change in pentane- or toluene=insoluble constituents indicates a change in asphalt properties that could lead to problems in service. The insoluble constituents measured can also assist in evaluating the performance characteristics of asphalt.

Two test methods are used: Procedure A covers the determination of insoluble constituents without the use of coagulant in the pentane and provides an indication of the materials that can be readily separated from the diluted asphalt by centrifugation. Procedure B covers the determination of insoluble constituents in asphalt that contains additives and uses a coagulant. In addition to the materials separated by using procedure A, this coagulation procedure separates some finely divided materials that may be suspended in the asphalt. The results obtained by procedures A and B should not be compared because they usually give different values. The same procedure should be applied when comparing results obtained periodically on asphalt in use or when comparing results determined in different laboratories.

In procedure A, a sample is mixed with pentane and centrifuged, after which the asphalt solution is decanted and the precipitate is washed twice with pentane, dried, and weighed. For toluene-insoluble constituents, a separate sample of the asphalt is mixed with pentane and centrifuged. The pre-

cipitate is washed twice with pentane, once with toluene-alcohol solution, and once with toluene. The insoluble material is then dried and weighed. In procedure B, procedure A is followed except that instead of pentane, a pentane-coagulant solution is used.

Many investigations of relationships between composition and properties take into account only the concentration of the asphaltenes, independent of any quality criterion. However, a distinction should be made between the asphaltenes that occur in straight-run asphalts and those that occur in blown asphalts. Because asphaltenes are a solubility class rather than a distinct chemical class vast differences occur in the makeup of this fraction when it is produced by different processes.

Finally, composition data should always be applied to in-service performance to properly evaluate the behavior of the asphaltic binder under true working conditions.

15.3.9. 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 15.6°C (60°F); (2) *relative density* is the ratio of the mass of a given volume of liquid at 15.6°C (60°F) to the mass of an equal volume of pure water at the same temperature; and (3) *specific gravity* is the same as 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 a 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.

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 a liquid at test temperatures between 15 and 35°C (59–95°F). This test method applies to petroleum oils with high vapor pressures pro-

vided that 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 (59–95°F) that have vapor pressures below 600 mmHg and viscosities below about 15,000 cSt at the temperature of 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 (ASTM D-287) is also 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 API gravity, which is derived from the specific gravity

$$\text{API gravity, deg} = (141.5/\text{sp gr } 60/60°\text{F}) - 131.5$$

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 by using a glass hydrometer for petroleum and petroleum products that are normally handled as liquids and 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 nonhydrocarbons 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).

For solid and semisolid asphalt a pycnometer is generally used (ASTM D-70), and a hydrometer is applicable to liquid asphalt (ASTM D-3142).

15.3.10. Distillation

Asphalt is prepared from a distillation residuum, and therefore the need for distillation data is limited. Vacuum distillation data (ASTM D-1160) will be valuable for composition purposes if the asphalt is prepared from an atmospheric residuum. Approximate amounts of volatile constituents can also be determined by test methods developed for other products (ASTM D-20, ASTM D-402, ASTM D-3607, ASTM D-4893) but that are particularly applicable to cutback asphalt.

Asphalt can also be examined for evaporative losses with a test method designed for grease (ASTM D-2595) or for engine oil (ASTM D-5480, ASTM D-5800, ASTM D-6375I, P 421). In another test method (ASTM D-972), the evaporative losses at any temperature in the range of l00–150°C (210–300°F) can be determined. A weighed sample is placed in an evaporation cell in an oil bath at the desired test temperature. Heated air at a specified flow rate is passed over the sample surface for 22 h, after which, the loss in sample mass is determined. In yet another method (ASTM D-2595), which is used to supplement the original method (ASTM D-972), the loss of volatile materials from a grease over a temperature range of 93–316°C (200–600°F) can be determined. This test uses an aluminum block heater, instead of an oil bath (ASTM D-972) to achieve higher temperatures.

Another test (ASTM D-6) allows the determination of the percent loss of mass when a weighed quantity of water-free material is heated in moving air for 5 h at 163°C (325°F). In this test method a gravity convection oven with a rotating shelf is used, and the method provides only a relative measurement of the volatility of a material under test conditions. It may be required for bituminous coating to be applied to galvanized, corrugated, culvert tube. A test for the loss of heating from a thin film is also available (ASTM D-1754).

15.3.11. Ductility

The *ductility* of asphalt is a measure of the flexibility of the asphalt and is expressed as the distance in centimeters that a standard briquette can be elongated before breaking (ASTM D-113, IP 32). Ductility is a combination of flow properties and reflects homogeneity, cohesion, and shear susceptibility; it is an indication of fatigue life and cracking.

15.3.12. Durability

The *durability* of asphalt is an indication of the presence of the necessary chemical and physical properties required for the specified pavement performance. The property indicates the resistance of the asphalt to change during the in-service conditions that are prevalent during the life of the pavement. The durability is determined in terms of resistance to oxidation (resistance to weathering) and water resistance (ASTM D-529, ASTM D-1669, ASTM D-1670, ASTM E-42).

15.3.13. Elemental Analysis

Asphalt is not composed of a single chemical species but is rather a complex mixture of organic molecules that vary widely in composition and are composed of carbon, hydrogen, nitrogen, oxygen, and sulfur as well as trace amounts of metals, principally vanadium and nickel. The heteroatoms, although a minor component compared with the hydrocarbon moiety, can vary in concentration over a wide range depending on the source of the asphalt and can be a major influence on asphalt properties.

Generally, most asphalt is 79–88% w/w carbon, 7–13% w/w hydrogen, trace–8% w/w sulfur, 2–8% w/w oxygen, and trace–3% w/w nitrogen. Trace metals such as iron, nickel, vanadium, calcium, titanium, magnesium, sodium, cobalt, copper, tin, and zinc occur in crude oils. Vanadium and nickel are bound in organic complexes and, by virtue of the concentration (distillation) process by which asphalt is manufactured, are also found in asphalt. The catalytic behavior of vanadium has prompted studies of the relation between vanadium content and an asphalt's sensitivity to oxidation (viscosity ratio). The significance of metals in the behavior of asphalts is not yet well understood or defined.

Thus elemental analysis is still of considerable value to determine the amounts of elements in asphalt, and the method chosen for the analysis may be subject to the peculiarities or character of the feedstock under investigation and should be assessed in terms of accuracy and reproducibility. The methods that are designated for elemental analysis are:

1. *Carbon* and *hydrogen content* (ASTM D-1018, ASTM D-3178, ASTM D-3343, ASTM D-3701, ASTM D-5291, ASTM E-777, IP 338);
2. *Nitrogen content* (ASTM D-3179, ASTM D-3228, ASTM D-3431, ASTM E-148, ASTM E-258, ASTM D-5291, and ASTM E-778);
3. *Oxygen content* (ASTM E-385); and
4. *Sulfur content* (ASTM D-124, ASTM D-129, ASTM D-139, ASTM D-1266, ASTM D-1552, ASTM D-1757, ASTM D-2622, ASTM D-2785, ASTM D-3120, ASTM D-3177, ASTM D-4045, ASTM D-4294, ASTM E-443, IP 30, IP 61, IP 103, IP 104, IP 107, IP 154, IP 243).

The determination of *nitrogen* has been performed regularly by the Kjeldahl method (ASTM D-3228), the Dumas method, and the microcoulometric method (ASTM D-3431). The chemiluminescence method is the most recent technique applied to nitrogen analysis for petroleum. The chemiluminescence method determines the amount of chemically bound nitrogen in liquid hydrocarbon samples. In this method, the samples are introduced to the oxygen-rich atmosphere of a pyrolysis tube maintained at 975°C (1785°F). Nitrogen in the sample is converted to nitric oxide during combustion, and the combustion products are dried by passage through magnesium perchlorate [$Mg(ClO_4)_2$] before entering the reaction chamber of a chemiluminescence detector.

Oxygen is one of the five (C, H, N, O, and S) major elements in asphalt, and although the level rarely exceeds 1.5 % by weight, it may still be critical to performance. Many petroleum products do not specify a particular oxygen content, but if the oxygen compounds are present as acidic compounds such as phenols (Ar-OH) and naphthenic acids (cycloalkyl-COOH), they are controlled in different specifications by a variety of tests.

15.3.14. Emulsified Asphalt

There is a standard test method (ASTM D-244) that covers a variety of tests for the composition, handling, nature and classification, storage, use, and specifying of asphalt emulsions used primarily for paving purposes.

15.3.15. Flash Point

The *flash point* is the lowest temperature at which application of a test flame causes the vapor of a sample to ignite under specified test conditions. The flash point measures the tendency of a sample to form a flammable mixture with air under controlled laboratory conditions. Flash point data are used in shipping and safety regulations to define *flammable* and *combustible* materials as well as to indicate the possible presence of highly volatile and

flammable material in a relatively nonvolatile or nonflammable material. The flash point should not be confused with auto-ignition temperature (ASTM E-659), which measures spontaneous combustion with no external source of ignition.

The Pensky–Martens closed tester (ASTM D-93, IP 34) and the tag closed tester (ASTM D-56) are normally used for determining the flash point of fuel oil and similar products. The Cleveland open cup method (ASTM D-92) is most commonly used, although the Tag open cup (ASTM D-3143) is applicable to cutback asphalt. As noted above, the flash point of asphalt is an indication of fire hazard and is frequently used to indicate whether asphalt has been contaminated with materials of lower flash point.

15.3.16. Float Test

The float test is used to determine the consistency of asphalt at as specified temperature.

One test method (ASTM D-139) is normally used for asphalt that is too soft for the penetration test (ASTM D-5, ASTM D-217, ASTM D-937, ASTM D-1403, IP 50, IP 179, IP 310).

15.3.17. Molecular Weight

The molecular weight of asphalt is not always (in fact, rarely) used in specifications. Nevertheless, there may be occasions when the molecular weight of asphalt is desired, hence the need to reference the various methods here.

Currently, of the methods available, several standard methods are recognized as being useful for determination of the molecular weight of petroleum fractions; these methods are:

ASTM D-2224: Test Method for Mean Molecular Weight of Mineral Insulating Oils by the Cryoscopic Method (discontinued in 1989 but still used by some laboratories for determining the molecular weight of petroleum fractions up to and including gas oil).

ASTM D-2502: Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils from Viscosity Measurements.

ASTM D-2503: Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure.

ASTM D-2878: Method for Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils.

ASTM D-3593: Test Method for Molecular Weight Averages/Distribution of Certain Polymers by Liquid Size Exclusion (Gel Permeation) Chromatography—GPC Using Universal Calibration (has also been adapted to the investigation of molecular weight distribution in petroleum fractions).

Each method has proponents and opponents because of assumptions made in the use of the method or because of the mere complexity of the sample and the nature of the inter- and intramolecular interactions. Before application of any one or more of these methods, consideration must be given to the mechanics of the method and the desired end result.

Methods for molecular weight measurement are also included in other more comprehensive standards (ASTM D-128, ASTM D-3712), and several indirect methods have been proposed for the estimation of molecular weight by correlation with other, more readily measured physical properties (Speight, 2000, 2001). They are satisfactory when dealing with the conventional type of crude oils or their fractions and products and when approximate values are desired.

The molecular weights of the individual fractions of asphalt have received more attention, and have been considered to be of greater importance, than the molecular weight of the asphalt itself (Speight, 2000, 2001). The components that make up the asphalt influence the properties of the material to an extent that is dependent on the relative amount of the component, the molecular structure of the component, and the physical structure of the component, which includes the molecular weight.

Asphaltenes have a wide range of molecular weights, from 500 to at least 2500, depending upon the method (Speight, 1994). Asphaltenes associate in dilute solution in nonpolar solvents, giving higher molecular weights than is actually the case on an individual molecule basis. The molecular weights of the resins are somewhat lower than those of the asphaltenes and usually fall within the range 500–1000. This is due not only to the absence of association but also to a lower absolute molecular size. The molecular weights of the oil fractions (i.e., the asphalt minus the asphaltenes and minus the resins) is usually less than 500, often 300–400.

15.3.18. Penetration

The penetration test provides one measure of the consistency and hardness of asphalt.

Several test methods are available for products such as grease (ASTM D-217, ASTM D-1403, IP 50, IP 310) and petrolatum (ASTM D-937, IP 179) that might be modified for asphalt. The more usual test for asphalt (ASTM D-5, IP 49) is a commonly used consistency test. It involves the determina-

tion of the extent to which a standard needle penetrates a properly prepared sample of asphalt under definitely specified conditions of temperature, load, and time (100-g load, 5 s). The distance that the needle penetrates in units of mm/10 measured from 0 to 300, is the penetration value. Soft asphalt has a high penetration value, and the converse is true for hard asphalt.

15.3.19. Rheology

Asphalt is a viscoelastic material whose rheological properties reflect crude type and, to a lesser extent, processing. The ability of asphalt to perform under many conditions depends on flow behavior. Asphalt films or coatings showing no appreciable change from original conditions are usually desired, that is, they should allow some structural movement without permanent deformation.

The viscosity of hydrocarbons and temperature are related by the Walther equation:

$$\log \log (100_{\eta o}) = a - m \log T$$

where $_{\eta o}$ is the limiting viscosity at low shear rates (ASTM D-5018), T is the absolute temperature, and *a* and *m* are constants reflecting the intercept level and slope (or measure of susceptibility of viscosity to temperature, respectively). On the other hand, the general relationship for viscosity, temperature, and shear rate is:

$$\log \log 100_{\eta o} (1 \times CD^N) = a - m \log T$$

where D is shear rate; C is a function of limiting viscosity, limiting slope, and other constants; and N is the limiting slope.

Typical profiles for the different general families of asphalts include cutbacks or liquid materials, paving asphalt cements and the harder roofing and industrial materials that are usually graded by softening point. At lower temperatures (60°C/140°F and lower) and/or higher shear rates, which are typical of asphalt service conditions after incorporation in a roof or pavement, semisolid and solid asphalts display an increasing elastic component that relates viscosity with shear rate. The constant high viscosity level at lower shear rates is the limiting viscosity. Viscosities in the area where viscosity changes with shear rate are generally termed apparent viscosities.

A number of viscometers have been developed for securing viscosity data at temperatures as low as 0°C (32°F). The most popular instruments in current use are the cone plate (ASTM D-3205), parallel plate, and cap-

illary instruments (ASTM D-2170, ASTM D-2171). The cone plate can be used for the determination of viscosities in the range of 10 to $>10^9$ Pa at temperatures of 0–70°C (32–158°F) and at shear rates from 10^{-3} to $10^2 s^{-1}$. Capillary viscometers are commonly used for the determination of viscosities at 60–135°C (140–275°F).

Tests recently developed for measurement of viscoelastic properties are directly usable in engineering relations. Properties can be related to the inherent structure of bituminous materials. The fraction of highest molecular weight, the asphaltenes, is dispersed within the asphalt and is dependent on the content and nature of the resin and oil fractions. Higher aromaticity of the oil fractions or higher temperatures leads to viscous (sol) conditions. A more elastic (gel) condition results from a more paraffinic nature and is indicated by large elastic moduli or, empirically, by a relatively high penetration at a given softening point. Empirically, the penetration index (PI) and penetration temperature susceptibility (PTS) have been used to measure the degree of dispersion.

Asphalt develops an internal structure with age, steric hardening, in which viscosity can increase on aging without any loss of volatile material. Those with a particularly high degree of gel structure exhibit thixotropy.

15.3.20. Softening Point

The softening point of asphalt may be defined as that temperature at which asphalt attains a particular degree of softness under specified conditions of test.

Asphalt does not go through a solid-liquid phase change when heated and therefore does not have true melting point. As the temperature is raised, asphalt gradually softens or becomes less viscous. For this reason, the determination of the softening point must be made by an arbitrary but closely defined method if the test values are to be reproducible. Softening point determination is useful in determining the consistency as one element in establishing the uniformity of shipments or sources of supply.

Several tests are available to determine the softening point of asphalt (ASTM D-36, ASTM D-61, ASTM D-2319, ASTM D-3104, ASTM D-3461, IP 58). In the test method (ASTM D-36, IP 58), a steel ball of specified weight is laid on a layer of sample contained in a ring of specified dimensions. The softening point is the temperature, during heating under specified conditions, at which the asphalt surrounding the ball deforms and contacts a base plate.

15.3.21. Stain

The stain index is a measure of the sweating tendency of asphalt and its homogeneity.

The test is used for oxidized asphalt. The test method (ASTM D-1328) is used to measure the amount of stain on paper or other cellulosic materials by asphalt. Variations of the cigarette paper stain procedure include the Barber stain; talc stain tests are also used.

15.3.22. Temperature-Volume Correction

Tables are provided (ASTM D-1250) to allow the conversion of volumes of asphaltic materials from one temperature to another or, as generally used, to adjust volumes to a temperature of 15.6°C (60°F). The value commonly taken for mean coefficient of expansion is 0.00036 in the range 15.6–121.1°C (60–250°F).

15.3.23. Thin Film Oven Test

The standard rolling thin film oven test (RTFOT) (ASTM D-2872) is used to simulate the short-term aging of the binders during the hot-mixing process and has the purpose of determining the hardening effect of heat and air on a static film of asphalt when exposed in a thin film. The procedure utilizes a moving film exposed for 75 min at 163°C (325°F).

15.3.24. Viscosity

The viscosity of asphalt is a measure of its flow characteristics. It is generally the most important controlling property for manufacture and for selection to meet a particular application.

A number of instruments are in common use with asphalt for this purpose. The vacuum capillary (ASTM D-2171) is commonly used to classify paving asphalt at 60°C (140°F). Kinematic capillary instruments (ASTM D-2170, ASTM D-4402) are commonly used in the 60–135°C (140–275°F) temperature range for both liquid and semisolid asphalts in the range of 30–100,000 cSt. Saybolt tests (ASTM D-88) are also used in this temperature range and at higher temperatures (ASTM E-102). At lower temperatures the cone and plate instrument (ASTM D-3205) has been used extensively in the viscosity range 1,000–1,000,000 P. Other techniques include use of the sliding plate microviscometer and the rheogoniometer.

15.3.25. Water Content

The presence of water in asphalt can seriously affect performance insofar as it can effect asphalt-aggregate interactions and asphalt adsorption (ASTM D-4469). The water content of asphalt can be determined by a test

method (ASTM D-95, IP 74) that uses distillation equipment fitted with a Dean and Stark receiver.

In the test, the sample is heated under reflux with a water-immiscible solvent, which codistills with the water in the sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still.

15.3.26. Weathering

This test (ASTM D-529) evaluates the relative weather resistance of asphalts used for protective coating applications, especially for roofing. No direct measure of outdoor life or service can be obtained from this test. Methods for preparing test panels (ASTM D-1669) and failure end point testing (ASTM D-1670) are available.

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CHAPTER

16

COKE

16.1. INTRODUCTION

Coke is a gray to black solid carbonaceous residue that is produced from petroleum during thermal processing; characterized by having a high carbon content (95%+ by weight) and a honeycomb type of appearance, and insoluble in organic solvents. (ASTM D-121) (Chapter 2) (Gruse and Stevens, 1960; Guthrie, 1967; Weissermel and Arpe, 1978; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Speight, 2000; Speight and Ozum, 2002).

Coke consists mainly of carbon (90–95%) and has a low mineral matter content (determined as ash residue). Coke is used as a feedstock in coke ovens for the steel industry, for heating purposes, for electrode manufacture, and for production of chemicals. The two most important categories are *green coke* and *calcinated coke*. This latter category also includes *catalyst coke* deposited on the catalyst during refining processes; this coke is not recoverable and is usually burned as refinery fuel.

16.2. PRODUCTION AND PROPERTIES

Petroleum coke is the residue left by the destructive distillation of petroleum residua. That formed in catalytic cracking operations is usually nonrecoverable, as it is often employed as fuel for the process.

Delayed coke (Table 16.1) is produced during the *delayed coking* process—a batch process—from vacuum residua (Chapter 2) (Speight and Ozum, 2002). The carbonization (thermal decomposition) reactions involve dehydrogenation, rearrangement, and condensation. Two of the common feedstocks are vacuum residues and aromatic oils.

In the delayed coker the feed enters the bottom of the fractionator, where it mixes with recycled liquid condensed from the coke drum effluent. It is then pumped through the coking heater to one of two coke drums through a switch valve. It is at 480–500°C. Cracking and polymerization take place in the coke drum in a nominal 24-h period. Coking is a batch operation carried out in two coke drums. Coking takes place in one drum in

Table 16.1. Description of Delayed Coke Carbon Forms

	Delayed Coke
Needle coke	Ribbonlike parallel-ordered anisotropic domains that can also occur as folded structures
Lenticular/granular	Lenticular anisotropic domains of various sizes that are not aligned parallel to the particle surface
Mixed layer	Ribbon and lenticular anisotropic domains of various sizes in curved and irregular layered arrangements
Sponge	Porous microstructure with walls that are generally anisotropic but with pores and walls that vary in size
Shot	Ribbon and lenticular anisotropic domains arranged in concentric patterns to form shotlike coke
Amorphous	Isotropic carbon form closely associated with parent liquor. Higher in volatile matter than incipient mesophase
Incipient mesophase	Initial stage of mesophase formation. Transition stage between amorphous and mesophase
Mesophase	Nemitic liquid crystals. Lower in volatile matter than incipient mesophase

Table 16.2. Description of Fluid Coke Carbon Forms

	Fluid Coke
Layered	Anisotropic carbon domains aligned in concentric layers parallel to the particle surface similar to an onion-like pattern
Nonlayered	Anisotropic domains are not aligned parallel to the particle surface
Aggregates	Fragments of anisotropic domains
Amorphous	Isotropic carbon form closely associated with parent liquor. Higher in volatile matter than incipient mesophase
Incipient mesophase	Initial stage of mesophase formation. Transition stage between amorphous and mesophase
Mesophase	Nemitic liquid crystals. Lower in volatile matter than incipient mesophase

24 h while decoking is carried out in the other drum. A complete cycle is 48 h. Coke is cut from the drum with high-pressure water. Large drums are 27 ft in diameter and 114 ft flange to flange.

Fluid coke (Table 16.2) is produced during the *fluid coking* process—a continuous process in which heated coker feeds are sprayed into a fluidized bed of hot coke particles that are maintained at 20–40 psi and 500°C (932°F) (Chapter 2) (Speight and Ozum, 2002). The feed vapors are cracked while

forming a liquid film on the coke particles. The particles grow by layers until they are removed and new seed coke particles are added.

Coke for the aluminum industry is calcined to less than 0.5% volatiles at 1300–1400°C (2372–2552°F) before it is used to make anodes.

Petroleum coke is used for a number of purposes, but its chief use is in the manufacture of carbon electrodes for aluminum refining, which requires a high-purity carbon low in ash and sulfur free; the volatile matter must be removed by calcining. In addition to its use as a metallurgical reducing agent, petroleum coke is used in the manufacture of carbon brushes, silicon carbide abrasives, and structural carbon (e.g., pipes and Rashig rings), as well as calcium carbide manufacture, from which acetylene is produced:

$$\text{coke} \rightarrow CaC_2$$

$$CaC_2 + H_2O \rightarrow HC{\equiv}CH$$

16.3. TEST METHODS

The test methods for coke are necessary for defining the coke as a fuel (for internal use in a refinery) or for other uses, particularly those test methods in which prior sale of the coke is involved. Specifications are often dictated by environmental regulations, if not by the purchaser of the coke.

The test methods outlined below are the methods that are usually applied to petroleum coke but should not be thought of as the only test methods. In fact, there are many test methods for coke (ASTM, 2000, Volume 05.06) and these test methods should be consulted when either more detail or a fuller review is required.

16.3.1. Ash

The ash content (that is, the ash yield, which is related to the mineral matter content) is one of the properties used to evaluate coke; it indicates the amount of undesirable residue present. Some samples of coke may be declared to have an acceptable ash content, but this varies with the intended use of the coke.

For the test method, the preparation and sampling of the analytical sample must neither remove nor add mineral matter (ASTM D-346). Improper dividing, sieving, and crushing equipment, and some muffle furnace lining material, can contaminate the coke and lead to erroneous results. In addition, a high sulfur content of the furnace gases, regardless of the source of the sulfur, can react with an alkaline ash to produce erratic results. To counteract such an effect, the furnace should be swept with air.

In the test method (ASTM D-4422), a sample of petroleum coke is dried, ground, and ashed in a muffle furnace at 700–775°C (1292–1427°F). The noncarbonaceous residue is weighed and reported as the percent by weight ash. As already noted, the ash must not be understood to be the same as the mineral content of the petroleum coke.

In addition, ashing procedures can be used as a preliminary step for determination of the trace elements in coke and, by inference, in the higher-boiling fractions of the crude oil. Among the techniques used for trace element determinations are flameless and flame atomic absorption (AA) spectrophotometry (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 is often a matter of individual preference.

16.3.2. Calorific Value (Heat of Combustion)

The calorific value (heat of combustion) is an important property, particularly for the petroleum products that are used for burning, heating, or similar usage. Knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat. Heat of combustion per unit of mass of coke is a critical property of coke intended for use as a fuel.

In one test method that is suitable for coke (ASTM D-3523), the sample is supported on surgical gauze and placed in a heated chamber that is open to air at the top. The temperature of this sample is compared with that of an equal reference quantity of surgical gauze contained in an identical chamber. Tests may be conducted for durations of 4–72 h or longer.

Other methods using an adiabatic bomb calorimeter (ASTM D-2015, ASTM D-5865) are also available.

When an experimental determination of heat of combustion is not available and cannot be made conveniently, an estimate might be considered satisfactory (ASTM D-6446). In this test method the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the

hydrogen content (ASTM D-5291), density (ASTM D-5004), and sulfur content (ASTM D-1552, ASTM D-3177, ASTM D-4239) of the sample are determined by experimental test methods, and the net heat of combustion is calculated with the values obtained by these test methods based on reported correlations.

16.3.3. Composition

The composition of petroleum coke varies with the source of the crude oil, but in general, large amounts of high-molecular-weight complex hydrocarbons (rich in carbon but correspondingly poor in hydrogen) make up a high proportion. The solubility of petroleum coke in carbon disulfide has been reported to be as high as 50–80%, but this is in fact a misnomer, because the coke is the insoluble honeycomb material that is the end product of thermal processes.

Carbon and hydrogen in coke can be determined by the standard analytical procedures for coal and coke (ASTM D-3178, ASTM D-3179). However, in addition to carbon, hydrogen, and metallic constituents, coke also contains considerable amounts of nitrogen and sulfur that must be determined before sale or use. These elements will appear as their respective oxides (NO_x, SO_x) when the coke is combusted, thereby causing serious environmental issues.

A test method (ASTM D-5291) is available for simultaneous determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants. There are at least three instrumental techniques available for this analysis, each based on different chemical principles. However, all involve sample combustion, components separation, and final detection.

In one of the variants of the method, a sample is combusted in an oxygen atmosphere and the product gases are separated from each other by adsorption over chemical agents. The remaining elemental nitrogen gas is measured by a thermal conductivity cell. Carbon and hydrogen are separately measured by selective infrared cells as carbon dioxide and water. In another variant of the method, a sample is combusted in an oxygen atmosphere, the product gases are separated from each other, and the three gases of interest are measured by gas chromatography. In the third variant of the method, a sample is combusted in an oxygen atmosphere, the product gases are cleaned by passage over chemical agents, and the three gases of interest are chromatographically separated and measured with a thermal conductivity detector.

The nitrogen method is not applicable too samples containing <0.75% by weight nitrogen or for the analysis of volatile materials such as gasoline, gasoline oxygenate blends, or aviation turbine fuels. The details of the method should be consulted along with those given in an alternate method

for the determination of carbon, hydrogen, and nitrogen in coal and coke (ASTM D-3179, ASTM D-5373).

A test method (ASTM D-1552) is available for sulfur analysis; the method covers three procedures applicable to samples boiling above 177°C (350°F) and containing not less than 0.06 mass % sulfur. Thus the method is applicable to most fuel oils, lubricating oils, residua, and coke, and coke containing up to 8% by weight sulfur can be analyzed. This is particularly important for cokes that originate from heavy oil and tar sand bitumen, where the sulfur content of the coke is usually at least 5% by weight.

In the iodate detection system (ASTM D-1552), the sample is burned in a stream of oxygen at a sufficiently high temperature to convert about 97% by weight of the sulfur to sulfur dioxide. The combustion products are passed into an absorber containing 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. As combustion proceeds, bleaching the blue color, more iodate is added. The sulfur content of the sample is calculated from the amount of standard iodate consumed during the combustion.

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. Most of the sulfur present is converted to sulfur dioxide that is then measured with an infrared detector after moisture and dust are removed by traps. The calibration factor is determined with standards approximating the material to be analyzed.

For the iodate method, chlorine in concentrations <1 mass % does not interfere. The isoprene rubber method can tolerate somewhat higher levels. Nitrogen when present at >0.1 mass % may interfere with the iodate method, the extent of interference being dependent on the types of nitrogen compounds as well as the combustion conditions. It does not interfere in the infrared method. The alkali and alkaline earth metals zinc, potassium, and lead do not interfere with either method.

Determination of the physical composition can be achieved by any of the test methods for determining the toluene-insoluble constituents of tar and pitch (ASTM D-4072, ASTM D-4312). Furthermore, a variety of samples can be used to give a gradation of soluble and insoluble fractions. The coke, of course, remains in the extraction thimble (Soxhlet apparatus), and the extracts are freed from the solvent and weighed to give percent by weight yield(s).

Finally, one aspect that can pay a role in compositional studies is the sieve (screening) analysis. As in all petroleum products, sampling is, or can be, a major issue. If it is not performed correctly and poor sampling is the result, erroneous and very misleading data can be produced by the analytical method of choice. For this reason, reference is made to standard procedures

such as the *Standard Practice for Collection and Preparation of Coke Samples for Laboratory Analysis* (ASTM D-346) and the *Standards Test Method for the Sieve Analysis of Coke* (ASTM D-293).

16.3.4. Density

The *density* (*specific gravity*) of coke has a strong influence on its future use and can affect the characteristics of products such as carbon and graphite.

The density (specific gravity) of coke can be conveniently measured by use of a pycnometer. In the test method (ASTM D-5004), the mass of the sample is determined directly and the volume is derived by determining the mass of liquid displaced when the sample is introduced into a pycnometer. Oil or other material sprayed on calcined petroleum coke to control dust will interfere. Such oil can be removed by flushing with a solvent, which also must be completely removed before the density determination.

The *real density* of coke is obtained when the particle size of the specimen is smaller than 75 mm. The real density (or the particle size) exerts a direct influence on the physical and chemical properties of the carbon and graphite products that are manufactured from the coke.

In the test method (ASTM D-2638), a sample is dried and ground to pass through a 75-mm screen. The mass of the volume is determined directly, and the volume is derived by the volume of helium displaced when the sample is introduced into a helium pycnometer. The ratio of the mass of the sample to the volume is reported as the real density.

The *vibrated bulk density* (VBD) is an indication of the porosity of calcined petroleum coke, which affects its suitability for use in pitch-bonded carbon applications. This property is strongly dependent on average particle size and range and tends to increase with decreasing coke size. In the test method (ASTM D-4292), the coke is crushed, 100 g is measured after vibration, and the bulk density is calculated. The procedure is limited to particles passing through a 6.68-mm opening sieve and retained on a 0.21-mm opening sieve.

16.3.5. Dust Control Material

Dust control material is applied to calcined coke to help maintain a dust-free environment. It adds weight to the coke and can have a negative effect on the quality of carbon and graphite artifacts made from the treated coke. Hence, a maximum amount may be specified.

In the test method (ASTM D-4930), a weighed dry representative sample of 6.3-mm maximum-sized coke is extracted with methylene chloride in a Soxhlet apparatus. The mass of the residue remaining after extraction and evaporation of the solvent is the mass of the dust control material. This test

method is limited to those materials that are soluble in a solvent (for example, methylene chloride) that can be used in a Soxhlet extraction type of apparatus. Toluene and methyl chloroform have also been found to give results equal to those of methylene chloride.

16.3.6. Hardness

The Hardgrove grindability index (HGI) (ASTM D-5003) is used to predict the ranking in industrial size mills used for crushing operations and is commonly used to determine the hardness of coal samples (ASTM D-409) (Speight, 1994). The rankings are based on energy required, feed rate, or both. With the introduction of petroleum coke in the coal market, this test method has been extended to the coke.. In the current context, the Hardgrove grindability index is also used to select raw petroleum coke and coals that are compatible with each other when milled together in a blend so that segregation of the blend does not occur during particle size reduction.

In the test method (ASTM D-5003), the coke sample is crushed to produce a high yield of particles passing a No. 16 sieve and retained on a No. 30 sieve. These particles are reduced in the Hardgrove grindability machine according to the test method for coal (ASTM D-409). The quantity of particles retained on a No. 200 sieve is used to calculate the Hardgrove grindability index of the sample. Both this test method and the test method for coal (ASTM D-409) produce the same results on petroleum coke samples.

16.3.7. Metals

The presence and concentration of various metallic elements in petroleum coke are major factors in the suitability of the coke for various uses.

In the test method (ASTM D-5056), a sample of petroleum coke is ashed (thermally decomposed to leave only the ash of the inorganic constituents) at 525°C (977°F). The ash is fused with lithium tetraborate or lithium metaborate. The melt is then dissolved in dilute hydrochloric acid, and the resultant solution is analyzed by atomic absorption spectroscopy to determine the metals in the sample. However, spectral interferences may occur when using wavelengths other than those recommended for analysis or when using multielement hollow cathode lamps.

This test method can be used in the commercial transfer of petroleum coke to determine whether a lot of coke meets the specifications. This method can analyze raw and calcined coke for the trace elements aluminum, calcium, iron, nickel, silicon, sodium, and vanadium. The inductively coupled plasma atomic emission spectroscopy (ICPAES) method (ASTM

D-5600; ASTM D-6357) is complementary to this method and can also be used for determination of metals in petroleum coke.

In the inductively coupled plasma atomic emission spectroscopy (ICPAES) method (ASTM D-5600), a sample of petroleum coke is ashed at 700°C (1292°F) and the ash is fused with lithium borate. The melt is dissolved in dilute hydrochloric acid, and the resultant solution is analyzed by inductively coupled plasma atomic emission spectroscopy with aqueous calibration standards. Because of the need to fuse the ash with lithium borate or other suitable salt, the fusibility of ash may need attention (ASTM D-1857).

The wavelength-dispersive X-ray spectroscopy method (ASTM D-6376) provides a rapid means of measuring metallic elements in coke and provides a guide for determining conformance to material specifications. A benefit of this method is that the sulfur content can also be used to evaluate potential formation of sulfur oxides, a source of atmospheric pollution. This test method specifically determines sodium, aluminum, silicon, sulfur, calcium, titanium, vanadium, manganese, iron, and nickel.

In this method, a weighed portion of a sample of coke is dried at 110°C (230°F)and crushed to pass a 200-mesh sieve, mixed with stearic acid, and then milled and compressed into a smooth pellet. The pellet is irradiated with an X ray beam, and the characteristic X rays of the elements analyzed are excited, separated, and detected by the spectrometer. The measured X ray intensities are converted to elemental concentration by using a calibration equation derived from the analysis of the standard materials. The Kα spectral lines are used for all of the elements determined by this test method. This test method is also applicable to the determination of additional elements provided that appropriate standards are available for use and comparison.

16.3.8. Proximate Analysis

In contrast to the elemental analysis, the proximate analysis of coke is the determination of the amount of mineral ash (ASTM D-3174), volatile matter (ASTM D-3175), water (moisture) (ASTM D-3173), and fixed carbon. The fixed carbon is a calculated value and is the result of the summation of mineral ash (% by weight), volatile matter (% by weight), and water (% by weight) subtracted from 100.

The fixed carbon has been suggested to be analogous to the carbon residue (ASTM D-189, ASTM D-524, ASTM D-4530, IP 13, IP 14I, IP 398), but caution is advised against the literal use of such a comparison. The tests do not have a similar technical basis, and the calculation of fixed carbon by summation and subtraction means that the ultimate answer is subject to the errors of each measurement.

As an enhancement or extension of the method for proximate analysis, the determination of the physical composition can be achieved by any of the test methods for determining the toluene-insoluble constituents of tar and pitch (ASTM D-4072, ASTM D-4312). Furthermore, a variety of samples can be used to give a gradation of soluble and insoluble fractions. The coke, of course, remains in the extraction thimble (Soxhlet apparatus), and the extracts are freed from the solvent and weighed to give percent by weight yield(s).

16.3.9. Sulfur

In addition to metallic constituents, coke also contains considerable amounts of sulfur (ASTM D-1552, ASTM D-3177, ASTM D-4239) that must be determined before sale or use.

A test method (ASTM D-1552) is available for sulfur analysis that covers three procedures applicable to samples boiling above 177°C (350°F) and containing not less than 0.06 mass % sulfur. Thus the method is applicable to most fuel oils, lubricating oils, residua, and coke, and coke containing up to 8% by weight sulfur can be analyzed. This is particularly important for cokes that originate from heavy oil and tar sand bitumen, in which the sulfur content of the coke is usually at least 5% by weight.

In the iodate detection system (ASTM D-1552), the sample is burned in a stream of oxygen at a sufficiently high temperature to convert about 97% by weight of the sulfur to sulfur dioxide. The combustion products are passed into an absorber containing 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. As combustion proceeds, bleaching the blue color, more iodate is added. The sulfur content of the sample is calculated from the amount of standard iodate consumed during the combustion.

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. Most of the sulfur present is converted to sulfur dioxide that is then measured with an infrared detector after moisture and dust are removed by traps. The calibration factor is determined with standards approximating the material to be analyzed.

For the iodate method, chlorine in concentrations <1 mass % does not interfere. The isoprene rubber method can tolerate somewhat higher levels. Nitrogen when present at >0.1 mass % may interfere with the iodate method; the extent of interference being dependent on the types of nitrogen compounds as well as the combustion conditions. It does not interfere in the infrared method. The alkali and alkaline earth metals, zinc, potassium, and lead do not interfere with either method.

16.3.10. Volatile Matter

The volatile matter in coke affects the density of coke particles and can affect artifacts produced from further processing of the coke. The volatile matter can be used in estimating the calorific value of coke.

This test method (ASTM D-6374) covers the determination of the volatile matter produced by pyrolysis or evolved when petroleum coke is subjected to the specific conditions of the test method.

In the test method, the volatile matter of a moisture-free petroleum coke sample is determined by measuring the mass loss of the coke when heated under the exact conditions of the test method (ASTM D-6374).

There are two sources of interferences in this test method—moisture and particle size. Moisture increases the mass loss, the moisture-free sample weight is decreased by the amount of moisture actually present in the test sample, and the particle size range of the analysis sample affects the volatile matter. The coarser the sample, the lower the reported yield of volatile matter. The method is not satisfactory for determining the content of dust control material , and samples with a thermal history above 600°C (1112°F) are excluded from this test.

In another test method (ASTM D-4421), volatile matter of a moisture-free petroleum coke is determined by measuring the mass loss of the coke when heated under the exact conditions of this procedure. Again, the particle size range of the sample affects the volatile matter insofar as coarser samples give rise to a lower yield of volatile matter. Samples with a thermal history above 600°C (1112°F) are excluded from the test, and the method is not satisfactory for determining the content of dust control material.

16.3.11. Water

Water (or moisture) in coke adds weight to coke, and knowledge of the water in the coke is important in the purchase and sale of green coke.

The test method (ASTM D-4931) presents two procedures. The *preparation procedure* is used when the petroleum coke sample contains free water. The sample is weighed and air dried to equilibrate it with the atmosphere. Determination of the residual moisture is then determined with the *drying oven method.* Air drying and residual moisture are combined to report gross moisture. The *drying oven method* is used in routine commercial practice when the sample does not contain free water. The sample is crushed to at least 25-mm (1 in.) top sieve size and divided into individual aliquots of at least 500 g. This test method covers both the preparation procedure for samples containing free water and the determination of the gross moisture content of green petroleum coke.

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CONVERSION FACTORS

1 atmosphere = 760 mmHg = 14.696 psi = 29.91 in. Hg
1 atmosphere = 1.0133 bars = 33.899 ft H_20
1 barrel (oil) = 42 gal = 5.6146 ft^3
1 barrel (water) = 350 lb at 60°F
1 barrel per day = 1.84 cm^3 per s
1 Btu = 778.26 ft-lb
1 centipoise × 2.42 = lb mass/(ft) (h), viscosity
1 centipoise × 0.000672 = lb mass/(ft) (s), viscosity
1 cubic foot = 28,317 cm^3 = 7.4805 gal
Density of water at 60°F = 0.999 gram/cm^3 = 62.367 lb/ft^3 = 8.337 lb/gal
1 gallon = 231 $in.^3$ = 3785.4 cm^3 = 0.13368 ft^3
1 horsepower-hour = 0.7457 kWh = 2544.5 Btu
1 horsepower = 550 ft-lb/s = 745.7 W
1 inch = 2.54 cm
1 meter = 100 cm = 1000 mm = 10^6 µm = 10^{10} angstroms (Å)
1 ounce = 28.35 g
1 pound = 453.59 g = 7000 grains
1 square mile = 640 acres

GLOSSARY

The following list represents a selection of definitions that are commonly used in reference to petroleum analysis and will be of use to the reader.

Accuracy: a measure of how close the test result will be to the true value of the property being measured; a relative term in the sense that systematic errors or biases can exist but be small enough to be inconsequential.

Acidity: the capacity of an acid to neutralize a base such as a hydroxyl ion (OH^-).

Acid number: a measure of the reactivity of petroleum with a caustic solution; given in terms of milligrams of potassium hydroxide that are neutralized by one gram of petroleum.

Acid sludge: the residue left after treating petroleum oil with sulfuric acid for the removal of impurities; a black, viscous substance containing the spent acid and impurities.

Additive: a material added to another (usually in small amounts) to enhance desirable properties or to suppress undesirable properties.

Adsorption: transfer of a substance from a solution to the surface of a solid, resulting in relatively high concentration of the substance at the place of contact; see also **Chromatographic adsorption**.

Air-blown asphalt: asphalt produced by blowing air through residua at elevated temperatures.

Albertite: a black, brittle, natural hydrocarbon possessing a conchoidal fracture and a specific gravity of approximately 1.1.

Alicyclic hydrocarbon: a compound containing carbon and hydrogen only that has a cyclic structure (e.g., cyclohexane); also collectively called naphthenes.

Aliphatic hydrocarbon (saturated): a compound containing carbon and hydrogen only that has either an open-chain structure (e.g., ethane, butane, octane) or a cyclic structure (e.g., cyclohexane) in which the full valency of carbon (4) is satisfied by another atom.

Aliphatic hydrocarbon (unsaturated): a compound containing carbon and hydrogen only that has either an open-chain struc-

ture (e.g., ethylene, butene) or a cyclic structure (e.g., cyclohexene) in which the full valency of carbon (4) is satisfied by another atom and by at least one multiple bond.

Aliquot: that quantity of material of proper size for measurement of the property of interest; test portions may be taken from the gross sample directly, but often preliminary operations such as mixing or further reduction in particle size are necessary.

Alkalinity: the capacity of a base to neutralize the hydrogen ion (H^+).

Alkylate: the product of an **alkylation** (q.v.) process.

Alkylation: in the petroleum industry, a process by which an olefin (e.g., ethylene) is combined with a branched-chain hydrocarbon (e.g., *iso*-butane); alkylation may be accomplished as a thermal or as a catalytic reaction.

Alumina (Al_2O_3): used in separation methods as an adsorbent and in refining as a catalyst.

American Society for Testing and Materials (ASTM): the official organization in the United States for designing standard tests for petroleum and other industrial products.

Aniline point: the temperature, usually expressed in °F, above which equal volumes of a petroleum product and aniline are completely miscible; a qualitative indication of the relative proportions of paraffins in a petroleum product that are miscible with aniline only at higher temperatures; a high aniline point indicates low aromatics.

Analytical equivalence: the acceptability of the results obtained from the different laboratories; a range of acceptable results.

API gravity: a measure of the *lightness* or *heaviness* of petroleum that is related to density and specific gravity.

$$°\text{API} = (141.5/\text{sp gr @ } 60°\text{F}) - 131.5$$

Apparent bulk density: the density of a catalyst as measured; usually loosely compacted in a container.

Apparent viscosity: the viscosity of a fluid, or several fluids flowing simultaneously, measured in a porous medium (rock) and subject to both viscosity and permeability effects; also called **effective viscosity**.

Aromatic hydrocarbon: a hydrocarbon characterized by the presence of an aromatic ring or condensed aromatic rings; benzene and substituted benzene, naphthalene and substituted naphthalene, phenanthrene and substituted phenanthrene, as well as the higher condensed ring systems; compounds that are distinct from those of

aliphatic hydrocarbon (q.v.) or **alicyclic hydrocarbon** (q.v.).

Aromatization: the conversion of nonaromatic hydrocarbons to aromatic hydrocarbons by (1) rearrangement of **aliphatic** (noncyclic) **hydrocarbons** (q.v.) into aromatic ring structures and (2) dehydrogenation of alicyclic hydrocarbons (naphthenes).

Asphalt: the nonvolatile product obtained by distillation and subsequent treatment of the residuum of an asphaltic crude oil; a manufactured product.

Asphaltene fraction (asphaltenes): the brown to black powdery material produced by treatment of petroleum, petroleum residua, or bituminous materials with a low-boiling liquid hydrocarbon, e.g., pentane or heptane; soluble in benzene (and other aromatic solvents), carbon disulfide, and chloroform (or other chlorinated hydrocarbon solvents).

Asphaltene association factor: the number of individual asphaltene species that associate in nonpolar solvents as measured by molecular weight methods; the molecular weight of asphaltenes in toluene divided by the molecular weight in a polar nonassociating solvent, such as dichlorobenzene, pyridine, or nitrobenzene.

Asphaltic pyrobitumen: see **Asphaltoid**.

Asphaltite: a variety of naturally occurring dark brown to black, solid, nonvolatile bituminous material that is differentiated from bitumen primarily by a high content of material insoluble in *n*-pentane (asphaltene) or other liquid hydrocarbons.

Asphaltoid: a group of brown to black, solid bituminous materials the members of which are differentiated from asphaltites by their infusibility and low solubility in carbon disulfide.

Asphaltum: see **Asphalt**.

Associated molecular weight: the molecular weight of asphaltenes in an associating (nonpolar) solvent such as toluene.

Atmospheric residuum: a **residuum** (q.v.) obtained by distillation of a crude oil under atmospheric pressure, which boils above 350°C (660°F).

Atmospheric equivalent boiling point (AEBP): a mathematical method of estimating the boiling point at atmospheric pressure of nonvolatile fractions of petroleum.

Attapulgus clay: see **Fuller's earth**.

Average particle size: the weighted average particle diameter of a catalyst.

Barrel: the unit of measurement of liquids in the petroleum industry; equivalent to 42 U.S. standard gallons or 33.6 imperial gallons.

Base number: the quantity of acid, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample to a specified end point.

Basic nitrogen: nitrogen (in petroleum) that occurs in pyridine form.

Basic sediment and water (BS&W, BSW): the material that collects in the bottom of storage tanks, usually composed of oil, water, and foreign matter; also called **bottoms**.

Baumé gravity: the specific gravity of liquids expressed as degrees on the Baumé (°Bé) scale; for liquids lighter than water:

$$\text{Sp gr } 60°\text{F} = 140/(130 + °\text{Bé})$$

and for liquids heavier than water:

$$\text{Sp gr } 60°\text{F} = 145/(145 - °\text{Bé})$$

Bauxite: mineral matter used as a treating or chromatographic agent; hydrated aluminum oxide formed by the chemical weathering of igneous rocks.

Bbl: see **Barrel**.

Bentonite: montmorillonite (a magnesium-aluminum silicate); used as a treating agent.

Benzene: a colorless aromatic liquid hydrocarbon (C_6H_6).

Benzin: a refined light naphtha used for extraction purposes.

Benzine: an obsolete term for light petroleum distillates covering the gasoline and naphtha range; see **Ligroine**.

Benzol: the general term that refers to commercial or technical (not necessarily pure) benzene; also the term used for aromatic naphtha.

Between-laboratory precision: see **Interlaboratory precision**, **Intermediate precision**, and **Precision**).

Billion: 1×10^9

Bitumen: a semisolid to solid hydrocarbonaceous material found filling pores and crevices of sandstone, limestone, or argillaceous sediments.

Bituminous: containing bitumen or constituting the source of bitumen.

Bituminous rock: see **Bituminous sand**.

Bituminous sand: a formation in which the bituminous material (see **Bitumen**) is found as a filling in veins and fissures in fractured rocks or impregnating relatively shallow sand, sandstone, and limestone strata; a sandstone reservoir that is impregnated with a heavy, viscous black petroleum-like material that cannot be retrieved through a well by conventional production techniques (see also **Tar sand**).

Black oil: any of the dark-colored oils; a term now often applied to **heavy oil** (q.v.).

Blown asphalt: the asphalt prepared by air blowing a **residuum** (q.v.) or an **asphalt** *(q.v.)*.

Boiling range: the range of temperature, usually determined at atmospheric pressure in standard laboratory apparatus, over which the distillation of an oil commences, proceeds, and finishes.

Bottoms: the liquid that collects in the bottom of a vessel (tower bottoms, tank bottoms) during distillation; also the deposit or sediment formed during storage of petroleum or a petroleum product; see also **Residuum** and **Basic sediment and water**.

British thermal unit: see **Btu**.

Bromine number: the number of *grams* of bromine absorbed by 100 g of sample, which indicates the percentage of double bonds in the material.

Bromine index: the number of *milligrams* of bromine that will react with 100 g of the sample; used mostly for stocks that have an unusually low olefin content.

Brønsted acid: a chemical species that can act as a source of protons.

Brønsted base: a chemical species that can accept protons.

BS&W: see **Basic sediment and water**.

Btu (British thermal unit): the energy required to raise the temperature of 1 lb of water 1° Fahrenheit.

Bubble point: the temperature at which incipient vaporization of a liquid in a liquid mixture occurs, corresponding with the equilibrium point of 0% vaporization or 100% condensation.

Bumping: the knocking against the walls of a still occurring during distillation of petroleum or a petroleum product that usually contains water.

Burning point: see **Fire point**.

Burning-quality index: an empirical numerical indication of the likely burning performance of a furnace or heater oil; derived from the **distillation profile** (q.v.) and the **API gravity** (q.v.), and generally recognizing the factors of paraffinicity and volatility.

C_1, C_2, C_3, C_4, C_5 fractions: a common way of representing fractions containing a preponderance of hydrocarbons having 1, 2, 3, 4, or 5 carbon atoms, respectively, and without reference to hydrocarbon type.

Carbene: the pentane- or heptane-insoluble material that is insoluble in benzene or toluene but is soluble in carbon disulfide (or pyridine); a type of rifle used for hunting bison.

Carboid: the pentane- or heptane-insoluble material that is insoluble in benzene or toluene and is also insoluble in carbon disulfide (or pyridine).

Carbon-forming propensity: see **Carbon residue**.

Carbonizable material: constituents of a petroleum product that form a carbonaceous residue when treated with sulfuric acid.

Carbonization: the conversion of an organic compound into char or coke by heat in the substantial absence of air; often used in reference to the destructive distillation (with simultaneous removal of distillate) of coal.

Carbon rejection: upgrading processes in which coke is produced, e.g., coking.

Carbon residue: the amount of carbonaceous residue remaining after thermal decomposition of petroleum, a petroleum fraction, or a petroleum product in a limited amount of air; also called the *coke- or carbon-forming propensity*; often prefixed by the terms Conradson or Ramsbottom in reference to the inventors of the respective tests.

Catalyst: a chemical agent that, when added to a reaction (process) will enhance the conversion of a feedstock without being consumed in the process.

Catalyst selectivity: the relative activity of a catalyst with respect to a particular compound in a mixture, or the relative rate in competing reactions of a single reactant.

Catalytic cracking: the conversion of high-boiling feedstocks into lower-boiling products by means of a catalyst that may be used in a fixed bed (q.v.) or fluid bed (q.v).

Cat cracking: see **Catalytic cracking**.

Cetane index: an approximation of the **cetane number** (q.v.) calculated from the **density** (q.v.) and **mid-boiling point** (q.v.); see also **Diesel index**.

Cetane number: a number indicating the ignition quality of diesel fuel; a high cetane number represents a short ignition delay time; the ignition quality of diesel fuel can also be estimated from the following formula:

$$\text{diesel index} = [\text{aniline point } (^\circ\text{F}) \times \text{API gravity}]/100$$

Characterization factor: the UOP characterization factor K, defined as the ratio of the cube root of the molal average boiling point, T_B, in degrees Rankine ($^\circ R = {}^\circ F + 460$), to the specific gravity at 60°F/60°F:

$$K = (T_B)^{1/3}/\text{sp gr}$$

which ranges from 12.5 for paraffinic stocks to 10.0 for the highly aromatic stocks; also called the Watson characterization factor.

Chelating agents: complexforming agents with the ability to solubilize heavy metals.

Chemical octane number: the octane number added to gasoline by refinery processes or by the use of **octane number** (q.v.)

improvers such as tetraethyl lead.

Chromatographic adsorption: selective adsorption on materials such as activated carbon, alumina, or silica gel; liquid or gaseous mixtures of hydrocarbons are passed through the adsorbent in a stream of diluent, and certain components are preferentially adsorbed.

Chromatography: a method of separation based on selective adsorption; see also **Chromatographic adsorption**.

Clay: silicate minerals that also usually contain aluminum and have particle sizes less than 0.002 μm; used in separation methods as an adsorbent and in refining as a catalyst.

Cloud point: the temperature at which paraffin wax or other solid substances begin to crystallize or separate from the solution, imparting a cloudy appearance to the oil when the oil is chilled under prescribed conditions.

Coal: an organic rock.

Coal tar: the specific name for the **tar** (q.v.) produced from coal.

Coal tar pitch: the specific name for the **pitch** (q.v.) produced from coal.

Coke: a gray to black solid carbonaceous material produced from petroleum during thermal processing; characterized by having a high carbon content (95%+ by weight) and a honeycomb type of appearance and insoluble in organic solvents.

Coke number: used, particularly in Great Britain, to report the results of the **Ramsbottom carbon residue** test (q.v.), which is also referred to as a coke test.

Coker: the processing unit in which coking takes place.

Coking: a process for the thermal conversion of petroleum in which gaseous, liquid, and solid (coke) products are formed.

Color stability: the resistance of a petroleum product to color change caused by light, aging, etc.

Combustible liquid: a liquid with a flash point in excess of 37.8°C (100°F) but below 93.3°C (200°F).

Composition: the general chemical makeup of petroleum.

Composition map: a means of illustrating the chemical makeup of petroleum with chemical and/or physical property data.

Con Carbon (Conradson carbon residue): see **Carbon residue**.

Conradson carbon residue: see **Carbon residue**.

Contaminant: a substance that causes deviation from the normal composition of a product.

Conventional recovery: primary and/or secondary recovery; often

includes tertiary (enhanced) recovery methods.

Conversion: the thermal treatment of petroleum that results in the formation of new products by the alteration of the original constituents.

Conversion factor: the percentage of feedstock converted to light ends, gasoline, other liquid fuels, and coke,

Cracked residua: residua that have been subjected to temperatures above 350°C (660°F) during the distillation process.

Cracking: the thermal processes by which the constituents of petroleum are converted to lower-molecular-weight products.

Cracking temperature: the temperature (350°C/660°F) at which the rate of thermal decomposition of petroleum constituents becomes significant.

Crude assay: a procedure for determining the general distillation characteristics (e.g., **distillation profile**, q.v.) and other quality information of crude oil.

Crude oil: see **Petroleum (crude oil)**.

Crude still: **distillation** (q.v.) equipment in which crude oil is separated into various products.

Cut point: the boiling temperature division between distillation fractions of petroleum.

Cyclic hydrocarbons: see **Alicyclic hydrocarbon**

Cyclization: the process by which an open-chain hydrocarbon structure is converted to a ring structure, e.g., hexane to benzene.

Dealkylation: the removal of an alkyl group from aromatic compounds.

Deasphaltened oil: the fraction of petroleum after the asphaltenes have been removed.

Deasphaltening: removal of a solid powdery asphaltene fraction from petroleum by the addition of low-boiling liquid hydrocarbons such as *n*-pentane or *n*-heptane under ambient conditions.

Deasphalting: the removal of the asphaltene fraction from petroleum by the addition of a low-boiling hydrocarbon liquid such as *n*-pentane or *n*-heptane; more correctly, the removal of asphalt (tacky, semisolid) from petroleum (as occurs in a refinery asphalt plant) by the addition of liquid propane or liquid butane under pressure.

Decolorizing: removal of suspended, colloidal, and dissolved impurities from liquid petroleum products by filtering, adsorption, chemical treatment, distillation, bleaching, etc.

Dehydrating agents: substances capable of removing water (**drying**, q.v.) or the elements of water from another substance.

Delayed coking: a coking process in which the thermal reactions are allowed to proceed to com-

pletion to produce gaseous, liquid, and solid (coke) products.

Density: the mass (or weight) of a unit volume of any substance at a specified temperature; see also **Specific gravity**.

Desorption: the reverse process of adsorption whereby adsorbed matter is removed from the adsorbent; also used as the reverse of absorption (q.v.).

Desulfurization: the removal of sulfur or sulfur compounds from a feedstock.

Diesel fuel: fuel used for internal combustion in diesel engines; usually the fraction that distills after kerosene.

Diesel cycle: a repeated succession of operations representing the idealized working behavior of the fluids in a diesel engine.

Diesel index: an approximation of the **cetane number** (q.v.) of **diesel fuel** (q.v.) calculated from the **density** (q.v.) and **aniline point** (q.v.).

$$\text{diesel index} = \text{aniline point } (^\circ\text{F}) \times \text{API gravity}/100$$

Diesel knock: the result of a delayed period of ignition and the accumulation of diesel fuel in the engine.

Distillation: a process for separating liquids with different boiling points.

Distillation curve: see **Distillation profile**.

Distillation loss: the difference, in a laboratory distillation, between the volume of liquid originally introduced into the distilling flask and the sum of the residue and the condensate recovered.

Distillation profile: the distillation characteristics of petroleum and petroleum products showing the temperature and the percentage distilled.

Distillation range: the difference between the temperature at the initial boiling point and at the end point, as obtained by the distillation test.

Dropping point: the temperature at which grease passes from a semisolid to a liquid state under prescribed conditions.

Drying: removal of a solvent or water from a chemical substance; also referred to as the removal of solvent from a liquid or suspension.

Dry point: the temperature at which the last drop of petroleum fluid evaporates in a distillation test.

Ebullated bed: a process in which the catalyst bed is in a suspended state in the reactor by means of a feedstock recirculation pump that pumps the feedstock upward at sufficient speed to expand the catalyst bed at approximately 35% above the settled level.

Effective viscosity: see **Apparent viscosity**.

Engler distillation: a standard test for determining the volatility characteristics of a gasoline by measuring the percentage distilled at various specified temperatures.

Enhanced oil recovery: petroleum recovery after recovery by conventional (i.e., primary and/or secondary) methods (q.v.).

Entrained bed: a bed of solid particles suspended in a fluid (liquid or gas) at such a rate that some of the solid is carried over (entrained) by the fluid.

Ethanol: see **Ethyl alcohol (ethanol or grain alcohol)**.

Ethyl alcohol (ethanol or grain alcohol): an inflammable organic compound (C_2H_5OH) formed during fermentation of sugars; used as an intoxicant and as a fuel.

Evaporation: a process for concentrating nonvolatile solids in a solution by boiling off the liquid portion of the waste stream.

Expanding clays: clays that expand or swell on contact with water, e.g., montmorillonite.

Explosive limits: the limits of percentage composition of mixtures of gases and air within which an explosion takes place when the mixture is ignited.

Extractive distillation: the separation of different components of mixtures that have similar vapor pressures by flowing a relatively high-boiling solvent, which is selective for one of the components in the feed, down a distillation column as the distillation proceeds; the selective solvent scrubs the soluble component from the vapor.

FCC: **fluid catalytic cracking**.

Feedstock: petroleum, heavy oil, or bitumen as it is fed to the refinery; a refinery product that is used as the raw material for another process; the term is also generally applied to raw materials used in other industrial processes.

Filtration: the use of an impassable barrier to collect solids that allows liquids to pass.

Fire point: the lowest temperature at which, under specified conditions in standardized apparatus, a petroleum product vaporizes sufficiently rapidly to form above its surface an air-vapor mixture that burns continuously when ignited by a small flame.

Flammability range: the range of temperature over which a chemical is flammable.

Flammable: a substance that will burn readily.

Flammable liquid: a liquid with a flash point below 37.8°C (100°F).

Flammable solid: a solid that can ignite from friction or from heat remaining from its manufacture,

or which may cause a serious hazard if ignited.

Flash point: the lowest temperature to which the product must be heated under specified conditions to give off sufficient vapor to form a mixture with air that can be ignited by a flame.

Floc point: the temperature at which wax or solids separate as a definite floc.

Fluid catalytic cracking: cracking in the presence of a fluidized bed of catalyst.

Fluid coking: a continuous fluidized solids process that cracks feed thermally over heated coke particles in a reactor vessel to gas, liquid products, and coke.

Fly ash: particulate matter produced from mineral matter in coal that is converted during combustion to finely divided inorganic material and which emerges from the combustor in the gases.

Fractional composition: the composition of petroleum as determined by **fractionation** (separation) methods.

Fractional distillation: the separation of the components of a liquid mixture by vaporizing and collecting the fractions, or cuts, which condense in different temperature ranges.

Fractionating column: a column arranged to separate various fractions of petroleum by a single distillation, which may be tapped at different points along its length to separate various fractions in the order of their boiling points.

Fractionation: the separation of petroleum into constituent fractions with solvent or adsorbent methods; chemical agents such as sulfuric acid may also be used.

Fuel oil: also called **heating oil;** a distillate product that covers a wide range of properties.

Fuller's earth: a clay that has high adsorptive capacity for removing color from oils; attapulgus clay is a widely used fuller's earth.

Functional group: the portion of a molecule that is characteristic of a family of compounds and determines the properties of these compounds.

Gas oil: a petroleum distillate with viscosity and boiling range between those of kerosene and lubricating oil.

Gasoline: fuel for the internal combustion engine that is commonly, but improperly, referred to simply as "gas."

Gilsonite: an asphaltite that is >90% bitumen.

Glance pitch: an asphaltite.

Grahamite: an asphaltite.

Grease: a solid to semisolid product that is a lubricating fluid that has been gelled with a thickening agent so that the lubricant

can be retained more readily in the required area.

Green acids: water-soluble products from the refining of mineral (white) oil

Gum: an insoluble, tacky semisolid material formed as a result of the storage instability and/or the thermal instability of petroleum and petroleum products.

Heating oil: see **Fuel oil**.

Heavy ends: the highest-boiling portion of a petroleum fraction; see also **Light ends**.

Heavy fuel oil: fuel oil with a high density and viscosity; generally residual fuel.)

Heavy oil: petroleum having an API gravity of less than 20°; petroleum that is recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques.

Heavy petroleum: see **Heavy oil**.

Heteroatom compounds: chemical compounds that contain nitrogen and/or oxygen and/or sulfur and /or metals bound within their molecular structure(s).

Homogeneity: the degree to which a property or substance is randomly distributed throughout a material; homogeneity depends on the size of the units under consideration. A mixture of two solids may be inhomogeneous at the molecular or atomic level but homogeneous at the particulate level.

Hot filtration test: a test for the stability of a petroleum product.

Hydrocarbon compounds: chemical compounds containing only carbon and hydrogen.

Hydrocarbon-producing resource: a resource such as coal and oil shale (kerogen) that produces derived hydrocarbons by the application of conversion processes; the hydrocarbons so produced are not naturally occurring materials.

Hydrocarbon resource: resources such as petroleum and natural gas that can produce naturally occurring hydrocarbons without the application of conversion processes.

Hydroconversion: a term often applied to **hydrocracking** (q.v.)

Hydrocracking: a catalytic high-pressure, high-temperature process for the conversion of petroleum feedstocks in the presence of fresh and recycled hydrogen; carbon-carbon bonds are cleaved in addition to the removal of heteroatomic species.

Hydrogen addition: an upgrading process in the presence of hydrogen, e.g., hydrocracking; see **Hydrogenation**.

Hydrogenation: the chemical addition of hydrogen to a material. In nondestructive hydrogenation,

hydrogen is added to a molecule only if, and where, unsaturation with respect to hydrogen exists.

Hydrogen transfer: the transfer of inherent hydrogen within the feedstock constituents and products during processing.

Hydroprocessing: a term often equally applied to **hydrotreating** (q.v.) and **hydrocracking** (q.v.); also often collectively applied to both.

Hydrotreating: the removal of heteroatomic (nitrogen, oxygen, and sulfur) species by treatment of a feedstock or product at relatively low temperatures in the presence of hydrogen.

Ignitability: characteristic of liquids whose vapors are likely to ignite in the presence of ignition source; also characteristic of nonliquids that may catch fire from friction or contact with water and that burn vigorously.

Immiscible: two or more fluids that do not have complete mutual solubility and coexist as separate phases.

Incompatibility: the *immiscibility* of petroleum products and also of different crude oils that is often reflected in the formation of a separate phase after mixing and/or storage.

Increment: an individual portion of material collected by a single operation of a sampling device, from parts of a lot separated in time or space. Increments may be either tested individually or combined (composited) and tested as a unit.

Individuals: conceivable constituent parts of the population.

Initial boiling point: the temperature recorded when the first drop of liquid falls from the end of the condenser.

Initial vapor pressure: the vapor pressure of a liquid of a specified temperature and zero percent evaporated.

Instability: the inability of a petroleum product to exist for periods of time without change to the product.

Interlaboratory precision: the variability between test results obtained on the aliquots of the same homogeneous material in different laboratories with the same test method (see also **Intermediate precision** and **Precision**).

Intermediate precision: the precision obtained when an assay is performed by multiple analysts using several instruments in one laboratory (see also **Interlaboratory precision** and **Precision**.

Iodine number: a measure of the iodine absorption by oil under standard conditions; used to indicate the quantity of unsaturated compounds present; also called *iodine value*.

Ion exchange: a means of removing cations or anions from solution onto a solid resin.

Isomerization: the conversion of a *normal* (straight-chain) paraffin hydrocarbon into an *iso* (branched-chain)-paraffin hydrocarbon with the same atomic composition.

Jet fuel: fuel meeting the required properties for use in jet engines and aircraft turbine engines.

Kaolinite: a clay mineral formed by hydrothermal activity at the time of rock formation or by chemical weathering of rocks with high feldspar content; usually associated with intrusive granite rocks with high feldspar content.

Kata-condensed aromatic compounds: Compounds based on linear condensed aromatic hydrocarbon systems, e.g., anthracene and naphthacene (tetracene).

Kerogen: a complex carbonaceous (organic) material that occurs in sedimentary rocks and shales; generally insoluble in common organic solvents.

Kerosene (kerosine): a fraction of petroleum that was initially sought as an illuminant in lamps; a precursor to diesel fuel.

K-factor: see **Characterization factor**.

Kinematic viscosity: the ratio of **viscosity** (q.v.) to density, both measured at the same temperature.

Laboratory sample: a sample, intended for testing or analysis, prepared from a gross sample or otherwise obtained. The laboratory sample must retain the composition of the gross sample.

Lamp burning: a test of burning oils in which the oil is burned in a standard lamp under specified conditions to observe the steadiness of the flame, the degree of encrustation of the wick, and the rate of consumption of the kerosene.

Lamp oil: see **Kerosene**.

Lewis acid: a chemical species that can accept an electron pair from a base.

Lewis base: a chemical species that can donate an electron pair.

Light ends: the lower-boiling components of a mixture of hydrocarbons; see also **Heavy ends**, **Light hydrocarbons**.

Light hydrocarbons: hydrocarbons with molecular weights less than that of heptane (C_7H_{16}).

Light oil: the products distilled or processed from crude oil up to, but not including, the first lubricating oil distillate.

Light petroleum: petroleum with an API gravity greater than 20°.

Ligroine (Ligroin): a saturated petroleum naphtha boiling in the range of 20–135°C (68–275°F)

and suitable for general use as a solvent; also called **benzine** or **petroleum ether**.

Liquefied petroleum gas (LPG): propane, butane, or mixtures thereof, gaseous at atmospheric temperature and pressure, held in the liquid state by pressure to facilitate storage, transport, and handling.

Liquid petrolatum: see **White oil**.

Lot: a quantity of bulk material of similar composition whose properties are under study.

Lube: see **Lubricating oil**.

Lube cut: a fraction of crude oil of suitable boiling range and viscosity to yield lubricating oil when completely refined; also referred to as *lube oil distillates* or *lube stock*.

Lubricating oil: a fluid lubricant used to reduce friction between moving metal surfaces.

Mahogany acids: oil-soluble sulfonic acids formed by the action of sulfuric acid on petroleum distillates. They may be converted to their sodium soaps (mahogany soaps) and extracted from the oil with alcohol for use in the manufacture of soluble oils, rust preventives, and special greases. The calcium and barium soaps of these acids are used as detergent additives in motor oils.

Maltenes: the fraction of petroleum that is soluble in, for example, pentane or heptane; **deasphaltened oil** (q.v.); also the term arbitrarily assigned to the pentane-soluble portion of petroleum that is relatively high boiling (>300°C, 760 mm) (see also **Petrolenes**).

Mayonnaise: low-temperature petroleum sludge; a black, brown, or gray deposit with a soft, mayonnaise-like consistency; not recommended as a food additive!

Measurement: the means by which analytical data are produced with a specific test method.

Methanol: see **Methyl alcohol**.

Mercaptans: organic compounds with the general formula R-SH.

Method validation: see **Validation**.

Methyl alcohol (methanol; wood alcohol): a colorless, volatile, inflammable, and poisonous alcohol (CH_3OH) traditionally formed by destructive distillation of wood or, more recently, as a result of synthetic distillation in chemical plants.

Micelle: the structural entity by which asphaltenes are dispersed in petroleum.

Microcarbon residue: the carbon residue determined with a thermogravimetric method. See also **Carbon residue**.

Mid-boiling point: the temperature at which approximately 50% of a material has distilled under specific conditions.

Middle distillate: distillate boiling between the kerosene and lubricating oil fractions.

Mineral oil: the older term for petroleum; the term was introduced in the nineteenth century as a means of differentiating petroleum (rock oil) from whale oil, which, at the time, was the predominant illuminant for oil lamps.

Mineral oil (white oil): colorless or very pale oils within the lubricating oil boiling range and viscosity that are used for medicinal (pharmaceutical) oils and technical purposes, the chief difference being degree of refining.

Minerals: naturally occurring inorganic solids with well-defined crystalline structures.

Mitigation: identification, evaluation, and cessation of potential impacts of a process product or by-product.

Modified naphtha insolubles (MNI): an insoluble fraction obtained by adding naphtha to petroleum; usually, adding paraffinic constituents modifies the naphtha; the fraction might be equated to asphaltenes *if* the naphtha is equivalent to *n*-heptane, but usually it is not

Molecular sieve: a synthetic zeolite mineral having pores of uniform size; it is capable of separating molecules, on the basis of their size, structure, or both, by absorption or sieving.

Naft: pre-Christian era (Greek) term for **naphtha** (q.v.).

Napalm: a thickened gasoline used as an incendiary medium that adheres to the surface it strikes.

Naphtha: a generic term applied to refined, partly refined, or unrefined petroleum products and liquid products of natural gas, the majority of which distill below 240°C (464°F); the volatile fraction of petroleum that is used as a solvent or as a precursor to gasoline.

Naphthenes: cycloparaffins.

Native asphalt: see **Bitumen**.

Natural asphalt: see **Bitumen**.

Natural gas: the naturally occurring gaseous constituents that are found in many petroleum reservoirs; there are also reservoirs in which natural gas may be the sole occupant.

Neutralization: a process for reducing the acidity or alkalinity of a waste stream by mixing acids and bases to produce a neutral solution; also known as **pH adjustment**.

Neutralization number: the weight, in milligrams, of potassium hydroxide needed to neutralize the acid in 1 g of oil; an indication of the acidity of an oil.

Nonasphaltic road oil: any of the nonhardening petroleum distillates or residual oils used as dust layers. They have sufficiently low

viscosity to be applied without heating and, together with asphaltic road oils (q.v.), are sometimes referred to as dust palliatives.

Non-Newtonian: a fluid that exhibits a change of viscosity with flow rate.

Octane barrel yield: a measure used to evaluate fluid catalytic cracking processes; defined as (RON + MON)/2 times the gasoline yield, where RON is the research octane number and MON is the motor octane number.

Octane number: a number indicating the antiknock characteristics of gasoline.

Oils (fraction): the portion of the **maltenes** (q.v.) that is not adsorbed by a surface-active material such as clay or alumina.

Oil sand: see **Tar sand**.

Oil shale: a fine-grained, impervious sedimentary rock that contains an organic material called kerogen.

Overhead: the portion of the feedstock that is vaporized and removed during distillation.

Oxidation: a process that can be used for the treatment of a variety of inorganic and organic substances.

Oxidized asphalt: see **Air-blown asphalt**.

Particle density: the density of solid particles.

Particulate matter: particles in the atmosphere or on a gas stream, which may be organic or inorganic and originate from a wide variety of sources and processes.

Particle size distribution: the particle size distribution (of a catalyst sample) expressed as a percentage of the whole.

Pericondensed aromatic compounds: compounds based on angular condensed aromatic hydrocarbon systems, e.g., phenanthrene, chrysene, picene, etc.

Petrol: a term commonly used in some countries for **gasoline**.

Petrolatum: a semisolid product, ranging from white to yellow in color, produced during refining of residual stocks; see **Petroleum jelly**.

Petrolenes: the term applied to that part of the pentane-soluble or heptane-soluble material that is low boiling (<300°C/<570°F, 760 mm) and can be distilled without thermal decomposition (see also **Maltenes**).

Petroleum (crude oil): a naturally occurring mixture of gaseous, liquid, and solid hydrocarbon compounds usually found trapped deep underground beneath impermeable cap rock and above a lower dome of sedimentary rock such as shale; most petroleum reservoirs occur in sedimentary rocks of marine, deltaic, or estuarine origin; recoverable in its natural state by conven-

tional oil well production methods including currently used enhanced recovery techniques.

Petroleum asphalt: see **Asphalt**.

Petroleum ether: see **Ligroine**.

Petroleum jelly: a translucent, yellowish to amber or white, hydrocarbon substance (m.p. 38–54°C) having almost no odor or taste; derived from petroleum and used principally in medicine and pharmacy as a protective dressing and as a substitute for fats in ointments and cosmetics; also used in many types of polishes and in lubricating greases, rust preventives, and modeling clay; obtained by dewaxing heavy lubricating-oil stocks.

Petroleum refinery: see **Refinery**.

Petroleum refining: a complex sequence of events that result in the production of a variety of products.

Petroporphyrins: see Prophyrins.

Phase separation: the formation of a separate phase that is usually the prelude to coke formation during a thermal process; the formation of a separate phase as a result of the instability/incompatibility of petroleum and petroleum products.

pH adjustment: neutralization.

Pitch: the nonvolatile, brown to black, semi-solid to solid viscous product from the destructive distillation of many bituminous or other organic materials, especially coal.

PNA: a polynuclear aromatic compound (q.v.).

Polar aromatics: resins; the constituents of petroleum that are predominantly aromatic in character and contain polar (nitrogen, oxygen, and sulfur) functions in their molecular structure(s).

Polynuclear aromatic compound: an aromatic compound having two or more fused benzene rings, e.g. naphthalene, phenanthrene.

PONA analysis: a method of analysis for paraffins (P), olefins (O), naphthenes (N), and aromatics (A).

Pooled standard deviation: a weighted average of individual estimates of the standard deviation.

Population: a generic term denoting any finite or infinite collection of individual things, objects, or events in the broadest concept; an aggregate determined by some property that distinguishes things that do and do not belong.

Porphyrins: organometallic constituents of petroleum that contain vanadium or nickel; the degradation products of chlorophylls that became included in the protopetroleum.

Pour point: the lowest temperature at which oil will pour or flow

when it is chilled without disturbance under definite conditions.

Precipitation number: the number of milliliters of precipitate formed when 10 ml of lubricating oil is mixed with 90 ml of petroleum naphtha of a definite quality and centrifuged under definitely prescribed conditions.

Precision: the variability between test results obtained on the same material, using a specific test method.

Primary oil recovery: oil recovery utilizing only naturally occurring forces.

Primary structure: the chemical sequence of atoms in a molecule.

Principal components analysis: an examination of set of data as points in *n*-dimensional space (corresponding to *n* original tests) that is used to determine (first) the direction that accounts for the biggest variability in the data (*first principal component*).

Propane asphalt: see **Solvent asphalt**.

Propane deasphalting: solvent deasphalting with propane as the solvent.

Protopetroleum: a generic term used to indicate the initial product formed by changes that have occurred to the precursors of petroleum.

Pyrobitumen: see **Asphaltoid**.

Pyrolysis: exposure of a feedstock to high temperatures in an oxygen-poor environment.

Pyrophoric: substances that catch fire spontaneously in air without an ignition source.

Quadrillion: 1×10^{15}

Quench: the sudden cooling of hot material discharging from a thermal reactor.

Raffinate: the portion of the oil that remains insoluble after treatment by a solvent.

Ramsbottom carbon residue: see **Carbon residue**

Reduced crude: a residual product remaining after the removal, by distillation or other means, of an appreciable quantity of the more volatile components of crude oil.

Reduction: the process of preparing one or more subsamples from a sample; the process by which hydrogen is added to feedstocks during hydrotreating and hydrocracking processes; removal of unsaturation by the addition of hydrogen.

Refinery: a series of integrated unit processes by which petroleum can be converted to a slate of useful (salable) products.

Refinery gas: a gas (or a gaseous mixture) produced as a result of refining operations.

Refining: the process(es) by which petroleum is distilled and/or converted by application of a

physical and chemical processes to form a variety of products.

Reformed gasoline: gasoline made by a reforming process.

Reid vapor pressure: a measure of the volatility of liquid fuels, especially gasoline.

Repeatability: the maximum permissible difference due to test error between two results obtained on the same material in the same laboratory.

Reproducibility (reproducibility interval): the maximum permissible difference between two results obtained on the same material by different laboratories that would be equaled or exceeded in the long run in only 1 case in 20 in the normal and correct operation of the method.

Research octane method: a test for determining the knock rating, in terms of octane numbers, of fuels for use in spark-ignition engines; see also **Motor octane method**.

Residual asphalt: see **Straight-run asphalt**.

Residual fuel oil: obtained by blending the residual product(s) from various refining processes with suitable diluent(s) (usually middle distillates) to obtain the required fuel oil grades.

Residual oil: see **Residuum**.

Residuum (resid; *pl.*: residua): the residue obtained from petroleum after nondestructive distillation has removed all the volatile materials from crude oil, e.g., an atmospheric (345°C/650°F+) residuum.

Resin: the portion of the **maltenes** (q.v.) that is adsorbed by a surface-active material such as clay or alumina; the fraction of deasphaltened oil that is insoluble in liquid propane but soluble in *n*-heptane.

Rock asphalt: bitumen that occurs in formations that have a limiting ratio of bitumen to rock matrix.

Sample a portion of a population or lot. It may consist of an individual or groups of individuals. The sample must be representative of the bulk material.

Sampling: the means by which a representative sample is obtained.

SARA separation: a method of fractionation by which petroleum is separated into saturates, aromatics, resins, and asphaltene fractions.

Saturates: paraffins and cycloparaffins (naphthenes).

Saybolt Furol viscosity: the time, in seconds (*Saybolt Furol Seconds, SFS*), for 60 ml of fluid to flow through a capillary tube in a Saybolt Furol viscometer at specified temperatures between 70 and 210°F; the method is appropriate for high-viscosity oils such as transmission, gear, and heavy fuel oils.

Saybolt Universal viscosity: the time, in seconds (*Saybolt Universal Seconds, SUS*), for 60 ml of fluid to flow through a capillary tube in a Saybolt Universal viscometer at a given temperature.

Secondary structure: the ordering of the atoms of a molecule in space relative to each other.

Sediment: an insoluble solid formed as a result of the storage instability and/or the thermal instability of petroleum and petroleum products.

Segment: a specifically demarked portion of a lot, either actual or hypothetical.

Selective solvent: a solvent that, at certain temperatures and ratios, will preferentially dissolve more of one component of a mixture than of another and thereby permit partial separation.

Separation process: a process in which the constituents of petroleum are separated, usually without thermal decomposition, e.g., distillation and deasphalting.

Slime: a name used for petroleum in ancient texts.

Sludge: a semisolid to solid product that results from the storage instability and/or the thermal instability of petroleum and petroleum products.

Smoke point: a measure of the burning cleanliness of jet fuel and kerosene and an indication of the aromatics content of an oil.

Solubility parameter: a measure of the solvent power and polarity of a solvent.

Solvent asphalt: the **asphalt** (q.v.) produced by solvent extraction of residua or by light hydrocarbon (propane) treatment of a **residuum** (q.v.) or an asphaltic crude oil.

Solvent deasphalting: a process for removing asphaltic and resinous materials from reduced crude oils, lubricating oil stocks, gas oils, or middle distillates through the extraction or precipitant action of low-molecular-weight hydrocarbon solvents; see also **Propane deasphalting**.

Solvent extraction: a process for separating liquids by mixing the stream with a solvent that is immiscible with part of the waste but that will extract certain components of the waste stream.

Solvent naphtha: a refined naphtha of restricted boiling range used as a solvent; also called petroleum naphtha, petroleum spirits.

Solvent refining: see **Solvent extraction**.

Sour crude oil: crude oil containing an abnormally large amount of sulfur compounds; see also **Sweet crude oil**.

Specification: the data that give adequate control of feedstock behavior or product quality.

Specific gravity: the mass (or weight) of a unit volume of any substance at a specified temperature compared with the mass of an equal volume of pure water at a standard temperature; see also **Density**.

Specimen: see **Aliquot**.

Stabilization: the removal of volatile constituents from a higher-boiling fraction or product (stripping); the production of a product that, for all intents and purposes, does not undergo any further reaction when exposed to the air.

Standard deviation: a measure of the scatter in a set of data that fits a Gaussian distribution; see also **Pooled standard deviation**.

Steam distillation: distillation in which vaporization of the volatile constituents is effected at a lower temperature by introduction of steam (*open steam*) directly into the charge.

Storage stability (or storage instability): the ability (inability) of a liquid to remain in storage over extended periods of time without appreciable deterioration as measured by gum formation and the depositions of insoluble material (sediment).

Straight-run asphalt: the **asphalt** (q.v.) produced by the distillation of asphaltic crude oil.

Straight-run products: products obtained from a distillation unit and used without further treatment.

Subsample: a portion taken from a sample. A **laboratory sample** (q.v.) may be a subsample of a gross sample; similarly, a test portion may be a subsample of a laboratory sample.

Sweet crude oil: crude oil containing little sulfur; see also **Sour crude oil**.

Synthetic crude oil (syncrude): a hydrocarbon product produced by the conversion of coal, oil shale, or tar sand bitumen that resembles conventional crude oil; can be refined in a **petroleum refinery** (q.v.).

Tar: the volatile, brown to black, oily, viscous product from the destructive distillation of many bituminous or other organic materials, especially coal; a name used for petroleum in ancient texts.

Tar sand: the several rock types that contain an extremely viscous hydrocarbon that is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques; see also **Bituminous sand**.

Tertiary structure: the three-dimensional structure of a molecule.

Test portion: see **Aliquot**.

Thermal coke: the carbonaceous residue formed as a result of

a noncatalytic thermal process; the Conradson carbon residue; the Ramsbottom carbon residue.

Thermal cracking: a process that decomposes, rearranges, or combines hydrocarbon molecules by the application of heat without the aid of catalysts.

Thermal process: any refining process that utilizes heat without the aid of a catalyst.

Thermal stability (thermal instability): the ability (inability) of a liquid to withstand relatively high temperatures for short periods of time without the formation of carbonaceous deposits (sediment or coke).

Topped crude: petroleum that has had volatile constituents removed up to a certain temperature, e.g., 250°C+ (480°F+) topped crude oil; not always the same as a **residuum** (q.v.).

Topping: the distillation of crude oil to remove light fractions only

Trace element: those elements that occur at very low levels in a given system.

Treatment: any method, technique, or process that changes the physical and/or chemical character of petroleum.

Trillion: 1×10^{12}

True boiling point (True boiling range): the boiling point (boiling range) of a crude oil fraction or a crude oil product under standard conditions of temperature and pressure.

Ultimate analysis: elemental composition.

Unassociated molecular weight: the molecular weight of asphaltenes in a nonassociating (polar) solvent such as dichlorobenzene, pyridine, or nitrobenzene.

Uncertainty: same as **standard deviation** (q.v.).

Universal viscosity: see **Saybolt Universal viscosity**.

Unstable: usually refers to a petroleum product that has more volatile constituents present or refers to the presence of olefin and other unsaturated constituents.

UOP characterization factor: see **Characterization factor**.

Upgrading: the conversion of petroleum to value-added salable products.

Vacuum distillation: **distillation** (q.v.) under reduced pressure.

Vacuum residuum: a **residuum** (q.v.) obtained by distillation of a crude oil under vacuum (reduced pressure); the portion of petroleum that boils above a selected temperature such as 510°C (950°F) or 565°C (1050°F).

Validation: the process of proving that an analytical method is acceptable for its intended purpose.

Viscosity: a measure of the ability of a liquid to flow or a measure of its resistance to flow; the force required to move a plane surface of area 1 m^2 over another parallel plane surface 1 m away at a rate of 1 m/s when both surfaces are immersed in the fluid.

VGC (viscosity-gravity constant): an index of the chemical composition of crude oil defined by the general relation between specific gravity (sg) at 60°F and Saybolt Universal viscosity (SUV) at 100°F:

$$a = 10sg - 1.0752 \log (SUV - 38)/10sg - \log (SUV - 38)$$

where the constant, a, is low for the paraffinic crude oils and high for the naphthenic crude oils.

VI (viscosity index): an arbitrary scale used to show the magnitude of viscosity changes in lubricating oils with changes in temperature.

Viscosity-gravity constant: see **VGC (viscosity-gravity constant)**.

Viscosity index: see **VI (viscosity index)**.

Watson characterization factor: see **Characterization factor**.

Wax appearance point: the temperature at which wax crystals begin to precipitate from a fuel.

Weathered crude oil: crude oil that, because of natural causes during storage and handling, has lost an appreciable quantity of its more volatile components; also indicates uptake of oxygen.

Wobbe index (or Wobbe number): the calorific value of a gas divided by the specific gravity.

Wood alcohol: see **Methyl alcohol**.

Zeolite: a crystalline aluminosilicate used as a catalyst and having a particular chemical and physical structure.

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