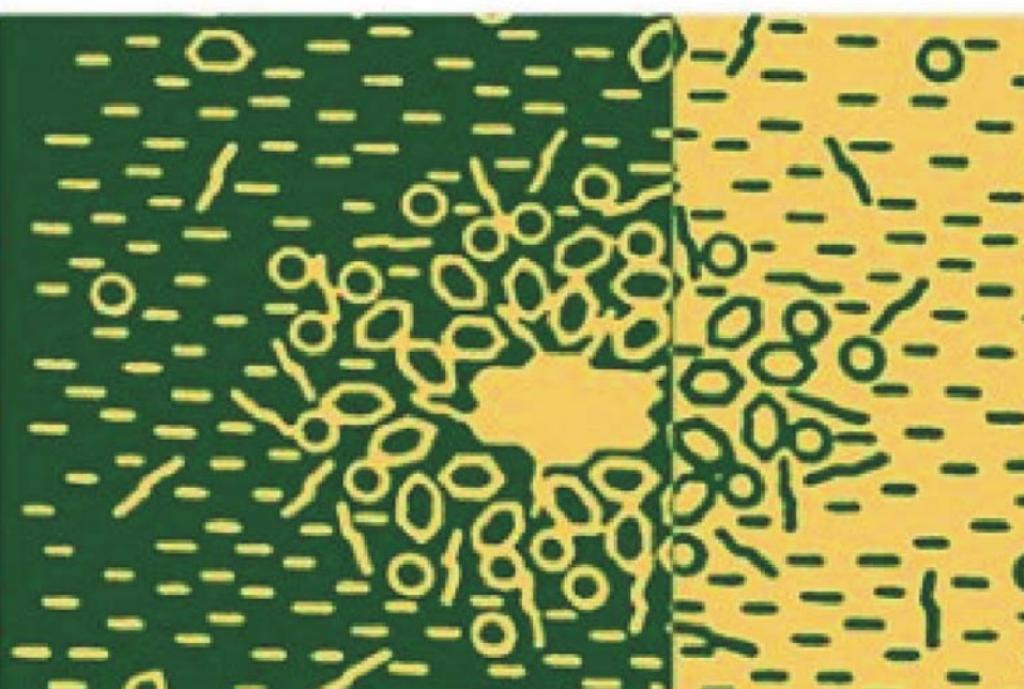


Chemical Analysis: A Series of Monographs on
Analytical Chemistry and its Applications
James B. Westerhout, Series Editor

Handbook of Petroleum Analysis

James G. Speight



Handbook of Petroleum Analysis

JAMES G. SPEIGHT

CD-WINC
Laramie, Wyoming



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PREFACE

Attempts to understand and manipulate chemical processes have persisted over centuries, with an explosion of technological innovation and research occurring in the last 100 years. The majority of these efforts have focused on using the knowledge gained to produce a useful product and achieve a perceived improvement in the performance of that product.

The laws of science will ultimately dictate what can or cannot be done with feedstocks to provide the needed products. The science of analytical chemistry is at the core of understanding of both the problems of processing various feedstocks. This book examines the way that the analytical science has been applied to defining the properties and behavior of the different feedstocks that are used in the petroleum refining industry.

In the twentieth century, scientists became increasingly well-versed in utilizing chemical knowledge to better understand the nature of petroleum, heavy oil, and tar sand bitumen and the influence of each feedstock on refining scenarios and on the product slate. Definitions of processing *do's* and *don't's* abound in the scientific and engineering literature, but the essence of these *rules* depends on analytical chemical measurements.

Petroleum exhibits a wide range of physical properties, and 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.

Evaluation of petroleum for use as a feedstock usually involves an examination of one or more of the physical properties of the material. By this means, a set of basic characteristics can be obtained that can be correlated with utility. Consequently, various standards organizations, such as the American Society for Testing and Materials in North America and the Institute of Petroleum in Great Britain have devoted considerable time and effort to the correlation and standardization of methods for the inspection and evaluation of petroleum and petroleum products.

The acceptance of heavier feedstocks (such as heavy oil and bitumen) by refineries has meant that the analytical techniques used for the lighter feedstocks

have had to evolve to produce meaningful data that can be used 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 feedstocks behavior during recovery operations.

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.

It is for these reasons that understanding the composition of petroleum, heavy oil, and bitumen as well as the chemical and physical properties of these feedstocks is extremely important.

An efficient evaluation of a feedstock or product requires the application of tests to insure that the feedstock or product meets specifications. These are then used to provide adequate control of product quality without being overrestrictive with the minimum of testing effort.

Product quality is judged by the performance during service. The performance of any product in particular service applications is therefore the ultimate criterion of quality. It is therefore necessary to find properties that allow assessment of the service performance, especially those tests that correlate closely with the service conditions. Sometimes the inspection tests attempt to measure these properties, for example, the research octane number test that was devised to measure the antiknock performance of motor fuel, or, in many cases, the significant property is obtained indirectly from the inspection test results.

However, where the specified property is not measured directly, it is important to ensure that a suitable combination of inspection tests is selected to give a high degree of correlation with the specified property.

Although the focus on this book is on the relevant ASTM test methods with the numbers given, where possible the corresponding IP test method number is also presented. As an aside, the ASTM or the IP may have withdrawn some of the tests noted herein. Nevertheless these methods are still included because of their continued use, for whatever reason, by analysts and also for historical (not hysterical) reference purposes!

Thus this book deals with the various aspects of petroleum analysis and provides a detailed explanation of the necessary standard tests and procedures that are applicable to feedstocks to help define predictability of behavior. In addition, the application of new methods for determining instability and incompatibility as well as analytical methods related to environmental regulations are described. More importantly, the book provides details of the meaning of the various test results

and how they might be applied to predict feedstock behavior. Where applicable, new tests that are not yet accepted as standard tests are described.

The focus of the book is the analysis of crude oil, with lesser emphasis on product analysis. Although product analysis is an extremely important aspect of petroleum science and technology, it is felt that the move to different feedstocks for refinery operations requires that more emphasis be placed on feedstock analysis and character, at least for this first text. Inclusion of product analyses is a natural extension of feedstock analysis, and they are included here but not as a separate section or sections.

Analytical chemists represent a rich resource for the various aspects of petroleum refining. Analytical chemists recognize that although the recent decades of experience have enhanced knowledge, they have also revealed large gaps in the kind of data needed to thoroughly understand the nature of petroleum refining.

The development of laboratory instrumentation over the last fifty years has been one of the forces shaping analytical standards, and improved instrumentation is already changing approaches to petroleum analysis. Like the twin strands of the famous DNA double helix, technology and analytical science and regulation will continue their closely linked relationship.

If this book helps toward a better understanding of the criteria for quality of petroleum and petroleum products and so leads to the writing of better specifications, it will have served its purpose.

DR. JAMES G. SPEIGHT

Laramie, Wyoming

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CHAPTER

1

DEFINITIONS AND HISTORY

1.1. INTRODUCTION

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

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.

Although not directly derived from composition, the terms *light* or *heavy* or *sweet* and *sour* provide convenient terms for use in descriptions. For example, *light petroleum* (often referred to as *conventional petroleum*) is usually rich in low-boiling constituents and waxy molecules 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. *Bitumen* is solid or near solid.

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 the idea 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* (page 5) 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.

The near-constancy of carbon and hydrogen contents is explained by the fact that variation in the amounts of each series of hydrocarbons does not have a profound effect on overall composition. The atomic ratio of hydrogen to carbon increases from the low- to the high-molecular-weight fractions. This is attributable to a decrease in the content of polynuclear aromatics and multiring cycloparaffins that are found in the higher-boiling fractious.

For higher-boiling feedstocks such as heavy oil and bitumen, the chemical composition becomes so complex and its relationship to performance so difficult to define that direct correlation may be impossible. In any case, simpler tests are required for quality control purposes. Analysis is then confined to the determination of certain important elements and to *characterization* of the feedstock in terms of a variety of structural groups.

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. 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 cause resistance to flow. Boiling-point distribution, density, and viscosity are easily measured and give a quick first evaluation of petroleum. 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 (Chapter 5) correlate better with molecular composition than density alone.

For heavy oil, bitumen, and residua, density and viscosity still are of great interest. But for such materials, hydrogen, nitrogen, sulfur, and metal content as well as carbon residue values become even more important (Table 1.1).

Table 1.1. Analytical Inspections for Petroleum, Heavy Oil, Bitumen, 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*
Distillation profile All fractions plus vacuum residue	Fractional composition: Asphaltenes, wt% Resins, wt% Aromatics, wt% Saturates, wt%

*Conradson carbon residue or microcarbon residue.

The acceptance of these heavy oils 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 used to assist in defining refinery scenarios for processing the feedstocks. In addition, selection of the most appropriate analytical procedures will aid in the predictability of feedstock behavior during refining. This same rationale can also be applied to feedstock behavior during recovery operations. Indeed, bitumen, a source of synthetic crude oil, is so different from petroleum (Table 1.2) (Speight and Moschopedis, 1979; Speight, 1990) 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,

Table 1.2. Properties of Conventional Crude Oil, Synthetic Crude Oil, and Bitumen

Property	Athabasca Bitumen	Synthetic Crude Oil	Conventional Crude Oil
Specific gravity	1.03	0.85	0.85–0.90
Viscosity, cp			
38°C/100°F	750,000	210	<200
100°C/212°F	11,300		
Pour point, °F	>50	−35	ca. −20
Elemental analysis (wt%):			
Carbon	83.0	86.3	86.0
Hydrogen	10.6	13.4	13.5
Nitrogen	0.5	0.02	0.2
Oxygen	0.9	0.00	<0.5
Sulfur	4.9	0.03	<2.0
Ash	0.8	0.0	0.0
Nickel (ppm)	250	0.01	<10.0
Vanadium (ppm)	100	0.01	<10.0
Fractional composition (wt%):			
Asphaltenes (pentane)	17.0	0.0	<10.0
Resins	34.0	0.0	<20.0
Aromatics	34.0	40.0	>30.0
Saturates	15.0	60.0	>30.0
Carbon residue (wt%):			
Conradson	14.0	<0.5	<10.0

lubricating 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, elastomers, and artificial fiber industries. Modern refining uses a sophisticated combination of heat, catalyst, and hydrogen to rearrange the petroleum constituents 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 to 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, the sheer volume involved has the potential

for environmental impact. Information on molecular composition is needed not only to identify the sources of contamination but also to understand the fate and effects of its potentially hazardous components.

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

Because of the complexity of the precursor mix that leads to the intermediate that is often referred to as *protopetroleum* and which eventually to petroleum, the end product contains an extremely wide range of organic functionality and molecular size. In fact, the variety is so great that it is unlikely that a complete compound-by-compound description for even a single crude oil would be possible. On the other hand, the molecular composition of petroleum can be described in terms of three classes of compounds: saturates, aromatics, and compounds bearing heteroatoms (nitrogen, oxygen, sulfur, and/or metals). Within each class, there are several families of related compounds. The distribution and characteristics of these molecular species account for the rich variety of crude oils.

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 mainly 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 the attempted classification of the petroleum. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of the significance of these properties.

Evaluation of petroleum for use as a feedstock usually involves an examination of one or more of the physical properties of the material. By this means, a set of basic characteristics can be obtained that can be correlated with utility.

Consequently, various standards organizations, such as the American Society for Testing and Materials (ASTM) in North America and the Institute of Petroleum (IP) in Britain have devoted considerable time and effort to the correlation and standardization of methods for the inspection and evaluation of petroleum and petroleum products.

It is for these reasons that understanding the composition of petroleum, heavy oil, and bitumen as well as the chemical and physical properties of these feedstocks is extremely important. However, product characteristics and specifications are also important.

Having decided what characteristics are necessary, it then remains to describe the sample in terms of a specification. This entails selecting suitable test methods and setting appropriate limits. Many specifications in widespread use have evolved 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.

Thus this book deals with the various aspects of petroleum analysis and provides a detailed explanation of the necessary standard tests and procedures that are applicable to feedstocks to help define predictability of behavior. In addition, the application of new methods for determining instability and incompatibility as well as analytical methods related to environmental regulations are described. More important, the book provides details of the meaning of the various test results and how they might be applied to predict feedstock behavior. Where applicable, new tests that are not yet accepted as standard tests are described.

1.2. DEFINITIONS

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

Because of 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 commonly used are illustrated here. Particularly troublesome, and more confusing, are those terms that are applied to the more viscous materials, for example, the use of the terms *bitumen* and *asphalt*. This part of the text

attempts to alleviate much of the confusion that exists, but it must be remembered that the terminology of petroleum is still open to personal choice and historical usage.

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, 1998; Speight, 1999a,b and references cited therein). The composition of petroleum varies with the source (Table 1.3).

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. 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

Table 1.3. Illustration of the Variation in Composition and Properties of Crude Oil

Crude Oil	Specific Gravity	API Gravity	Residuum > 1000 F
US 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

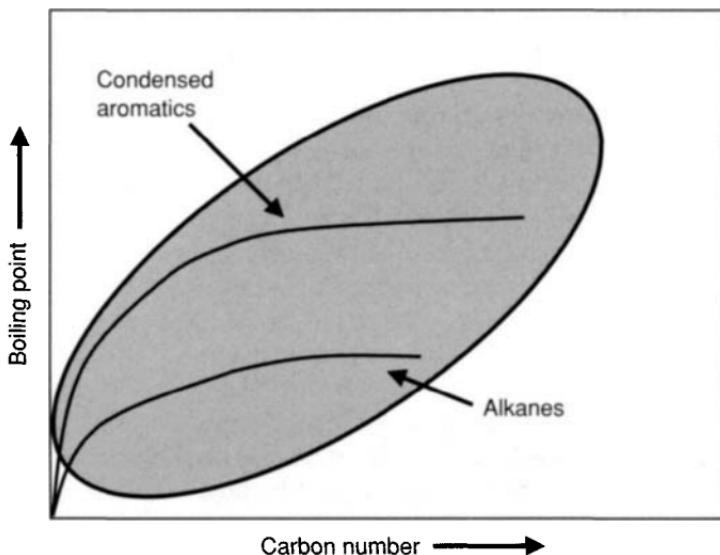


Figure 1.1. General boiling point–carbon number profile for petroleum.

nitrogen, oxygen, and sulfur, as well as metallic (porphyrin) constituents. However, the actual boundaries of such a *petroleum map* can only be defined arbitrarily 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 (Chapter 15) in a precise manner.

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 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* is the several rock types that contain an extremely viscous hydrocarbon that is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques.

More descriptively, tar sand is an unconsolidated to consolidated sandstone or 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 being 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* (Table 1.2), depends to a large degree on the composition and construction of the sands.

It must 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, i.e., a term that describes a material that is composed predominantly of carbon and hydrogen but recognizes 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 that cannot be recovered through a well by conventional oil well production methods including currently used enhanced recovery techniques; current methods involve mining for bitumen recovery (Speight, 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 (Table 1.4) approximates the boiling range of an atmospheric residuum and has a much lower proportion of volatile constituents than a conventional crude oil (Table 1.5).

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.

Table 1.4. Distillation Profile of Bitumen (Athabasca, McMurray Formation, Upper Cretaceous, Alberta, Canada) and Properties of the Fractions

Whole Bitumen	Boiling Range		Wt%	Cumulative Wt%	Specific Gravity	API Gravity	Sulfur Wt%	Carbon Residue (Conradson)
	°C	°F			1.030	5.9	5.8	19.6
Fraction*								
1	0–50	0–122	0.0	0.0				
2	50–75	122–167	0.0	0.0				
3	75–100	167–212	0.0	0.0				
4	100–125	212–257	0.0	0.0				
5	125–150	257–302	0.9	0.9				
6	150–175	302–347	0.8	1.7	0.809	43.4		
7	175–200	347–392	1.1	2.8	0.823	40.4		
8	200–225	392–437	1.1	3.9	0.848	35.4		
9	225–250	437–482	4.1	8.0	0.866	31.8		
10	250–275	482–527	11.9	19.9	0.867	31.7		
11	<200	<392	1.6	21.5	0.878	29.7		
12	200–225	392–437	3.2	24.7	0.929	20.8		
13	225–250	437–482	6.1	30.8	0.947	17.9		
14	250–275	482–527	6.4	37.2	0.958	16.2		
15	275–300	527–572	10.6	47.8	0.972	14.1		
Residuum	>300	>572	49.5	97.3				39.6

*Distillation at 762 mmHg and then at 40 mmHg for fractions 11–15.

Table 1.5. Distillation Profile or Crude Oil (Leduc, Woodbend, Upper Devonian, Alberta, Canada) and Properties of the Fractions

Whole Crude Oil	Boiling Range		Wt%	Cumulative Wt%	Specific Gravity	API Gravity	Sulfur Wt%	Carbon Residue (Conradson)
	°C	°F			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 mmHg then at 40 mmHg for fractions 11–15.

Table 1.6. 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)		Coke
Kerogen		
Coal		

*Bitumen from tar sand deposits.

†Products of petroleum processing.

For the purposes of terminology, it is preferable to subdivide petroleum and related materials into three major classes (Table 1.6):

materials that are of natural origin;
 materials that are manufactured; and
 materials that are integral fractions derived from the natural or manufactured products.

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 and liquids.

The *history* of any subject is the means by which the subject is studied in the hopes that much can be learned from the events of the past. In the current context, the occurrence and use of petroleum, petroleum derivatives (naphtha), heavy oil, and bitumen 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,b, 1959, 1964; James and Thorpe, 1994). Thus the use of petroleum and the development of related technology is not as modern a 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 BC by the people known as the Sumerians, who established one of the first great cultures of the civilized world. The Sumerians devised the cuneiform script, built the temple-towers known as 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 historic sites have confirmed the use of petroleum and bitumen in antiquity for construction, mummification, decorative jewelry, and waterproofing as well as medicinal use (Speight, 1978, 1999a). Many other references to bitumen occur throughout the Greek and Roman empires, and from then to the Middle Ages early scientists (alchemists) frequently referred to the use of bitumen. In the late fifteenth and early sixteenth centuries both Christopher Columbus and Sir Walter Raleigh have been credited with the discovery of the asphalt deposit on the island of Trinidad and apparently used the material to caulk their ships. There was also an interest in the thermal product of petroleum (nafta; naphtha) when it was discovered that this material could be used as an illuminant and as a supplement to asphalt incendiaries in warfare.

To continue such references is beyond the scope of this book, although they do give a flavor of the developing interest in petroleum. 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, a binder, or as a medicine. In this sense, documented history has not been kind to the scientist or engineer.

Thus the history of analysis of petroleum and its products 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 benzenesulfonic acids followed by fractional crystallization (de La Rue and Miller, 1857). 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 the history of 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.

Thus the stimulus given to petroleum science by new analytical approaches, either qualitative or quantitative, has been repeatedly observed. It is only recently that analytical chemistry has achieved recognition in keeping with its importance because the application of new techniques has resulted in new descriptive or theoretical knowledge.

Throughout the development of analytical chemistry, three objectives—*speed*, *selectivity*, and *sensitivity*—have been uppermost in the minds of chemists in designing new methods and improving or rejecting older methods. Ideally, and this is very true in the petroleum industry, an analytical method is most useful when it combines all three of these objectives. However, in practice, one or even two may be sacrificed when the third must be given unusual emphasis. For example, in the petroleum industry, the need to obtain results on-stream and without delay may dictate the use of methods not particularly noted for their sensitivity. Thus the purpose of the analysis frequently determines the choice of method.

One important aspect of petroleum analysis is the elemental composition. Liebig and Dumas so carefully laid the foundations of elemental organic analyses around 1830 that the methods underwent essentially no changes during the rest of the century except for minor modifications involving refinements in design and heating methods. This was particularly true in the case of carbon and hydrogen. However, in the case of nitrogen, there was a recognized need for a less intricate and time-consuming procedure than Dumas's method. In 1840, this method still required refinement with respect to the source of carbon dioxide, the degradation of nitrogen oxides, and the collection of nitrogen. Although these shortcomings were eliminated during the next two decades, the procedure was still complex and tedious. It was universally respected for reliability with all types of organic samples; but whenever other methods could be relied on to give accurate results, they were preferred.

Mineral matter in petroleum was, and is, generally determined by burning off the organic matter in a muffle furnace and weighing the ash. The ash might be further analyzed for individual elements by traditional inorganic methods. It was of course realized that the minerals in the sample were in a form that differed from the oxides, carbonates, sulfates, phosphates, and chlorides that made up the ash.

At the same time the concept of proximate analysis was being developed for coal, specifically, an analytical procedure that gave the amount of fixed carbon

under controlled conditions. This led to an interest in applying the test to the determination of the carbon residue produced by thermal treatment of petroleum. By inference, one might assume that the carbon residue test for petroleum was also based on the need to know the amount of volatile material produced during cracking.

Therefore, there were continuous attempts to develop methods for petroleum analysis from the modern inception of the industry in 1859 well into the twentieth century. Indeed, although qualitative tests had been used since antiquity, they were highly empirical and amounted to personal spot tests. As the result of the blossoming interest in reagents and reactions in the seventeenth century, there has been a continuing focus on numerous specific tests that have qualitative importance. This led to the development of a systematic basis for group separations, but it was not until the twentieth century that procedures became highly standardized.

The ASTM became active in developing standard tests for petroleum and petroleum products in 1904, from which evolved the Technical Committee D-2 on Petroleum Products and Lubricants with a scope that included almost all petroleum products. This evolution explains the designation of many standards for the evaluation of petroleum and petroleum products as ASTM D standards.

This large increase in the numbers of analytical methods applied to petroleum and petroleum products is, of course, made necessary by the greater attention to and need for reliable information concerning the composition of petroleum and its products. This information is increasingly requested in terms of individual hydrocarbons or certainly at a minimum in terms of type such as paraffinic, naphthenic, aromatic, olefinic, or combinations of these. However, the demand for these data could not have been met without real advances in the art and science of separating hydrocarbons and hydrocarbon types and the concurrent development of instrumental methods for determining physical, optical, and spectral properties with great accuracy and precision.

These developments, together with the fruits of the American Petroleum Institute Research Projects Nos. 6, 42, 44, 45, and 60 in making available both data on and samples of pure hydrocarbons for calibration purposes, have in effect marked the culmination of an era for analyses dependent primarily on fractionation, a few physical properties such as boiling point and density, and chemical reactions.

As a result of this work (Mair, 1960), it was recognized by 1925 or somewhat earlier that the hydrocarbons in petroleum belonged to several series, including normal paraffins, branched paraffins, cycloparaffins, and aromatics. For the cyclic paraffins, the presence of both five- and six-membered ring compounds was established. There was, however, at that time, no reasonably complete analysis of even the lower-boiling part of the gasoline fraction of any crude petroleum, and the manner in which the content of the individual constituents varied from crude to crude was virtually unknown.

During this time, the determination of functional groups, such as carboxyl, ester, unsaturated bonds, hydroxyl, and methoxyl, took on importance in connection with the establishment of the constitution of new organic compounds.

Perhaps the most common functional group is the carboxyl or organic acid group. When this group was present, titration with standard bases was the obvious method, and this procedure was commonly used. When a single acid of known identity was present, the procedure permitted direct analysis and also aided identification of pure acids whose identity was unknown, because the neutralization equivalent provided a guide to the molecular weight. The major drawback in the titration of organic acids was the fact that most such acids are weak and can only be titrated accurately by use of the correct indicator. A similar approach could be used with esters, where a carboxyl group is formed on hydrolysis.

Unsaturation was commonly detected by the decolorizing action of a compound on permanganate or bromine solutions. The ability of the double bond to absorb halogen was made the basis of a quantitative procedure.

The presence of hydroxyl groups was best determined by acetylation, followed by saponification of the ester, separation of the acetic acid by steam distillation, and titration.

Valuable as though they were, the chemical methods used in the early work on the composition of petroleum have generally been replaced by more modern methods. More recent progress has depended in part on the development of improved physical fractionating processes and in part on the development of new spectrographic methods of recognition. For distillation, laboratory columns of new design containing up to 200 or more theoretical stages of separation have become available. Such columns are capable of giving a fairly complete separation of hydrocarbons boiling less than 2°C apart. Improved procedures for azeotropic distillation have been developed. Spinning band columns and simulated distillation techniques now offer more information than was believed possible using the methods available in the middle decades of the twentieth century.

Adsorption methods have been developed for separating aromatic hydrocarbons quantitatively from paraffins and cycloparaffins; the same procedures will break down aromatic mixtures into mononuclear, dinuclear, and trinuclear portions. In certain cases, adsorption may be used to separate isomers, particularly aromatic isomers. An extension of the method of partition chromatography, which makes use of certain fluorochemicals as the mobile phase, is also effective for separating paraffins (particularly branched paraffins) from cycloparaffins. The same classes can also be separated using a partition chromatographic method with liquid displacement. A crystallization procedure for sorting out normal and branched paraffins and cyclic and aromatic hydrocarbons has come into wide use. This process depends on the formation of solid molecular compounds of the normal paraffins with urea, the separation of these compounds from the remaining liquid, and the regeneration of the normal paraffins. Fractionation by thermal diffusion has been

applied to petroleum fractions, particularly in the higher-boiling gas oil and lubricating oil ranges. The separation in this case appears to depend, in part at least, on the shapes of the component molecules. Where aromatics are absent, the separation is approximately according to cycloparaffin ring content and resembles that obtained with solvent extraction. Countercurrent solvent extraction has also been used principally as a means of separating the higher-boiling fractions according to hydrocarbon type.

Within recent years, molecular spectroscopy has been applied successfully to determining quantitatively the percentage of each hydrocarbon in mixtures. In some cases, spectroscopic methods are used to determine hydrocarbon types. For example, ultraviolet spectroscopy may determine aromatics and mass spectroscopy the content of paraffins, cycloparaffins, olefins, and aromatics in straight-run or cracked fractions in the gasoline range. Even for fractions from lubricating oil distillates (preferably separated as far as practical by other methods) high-temperature mass spectrometry gives useful information concerning the amounts of certain types of hydrocarbons and sulfur compounds. Infrared spectroscopy has also been applied in this molecular weight range to give values of, for example, the content of methyl groups as well as of methylene groups in long chains and in cycloparaffin rings.

Petroleum products are used for hundreds of different purposes with widely differing requirements; the criteria for quality are, therefore, numerous and complex. It is the purpose of this book to identify these criteria, to explain how they are met by suitable refining, and to describe how the quality is controlled by appropriate analysis and testing.

In summary, the nineteenth century was a period of consolidation in the field of chemical analysis from which petroleum analysis was born and benefited. This was important because it led to an understanding of the relationships of the various constituents for petroleum and hence to real and potential utility of this resource.

Instrumental methods were recognized as being important in analytical chemistry as the nineteenth century drew to a close. There were the awakenings of the potential role that instrumentation would play in process control.

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 6000 years of its use, the importance of petroleum has progressed from the relatively simple use of asphalt from Mesopotamian seepage sites to the present-day refining operations that yield a wide variety of products and petrochemicals (Speight, 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 have been made to formulate and standardize petroleum analysis.

As the twentieth century aged, 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 have 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. These instruments acquired simplicity of use that led to acquisitions by all laboratories involved in petroleum analysis.

Ultraviolet absorption, because of its use in studies of the structure of organic compounds, was particularly useful especially because the aromatic ring systems have a characteristic absorption that is used as a diagnostic value.

Perhaps the greatest advance in the use of instrumental techniques has been in the application of *infrared spectroscopy* to petroleum analysis. Instruments were available before 1920, but the real progress in infrared work occurred after 1940, when it became possible to relate certain bands in the spectra of petroleum and its derivatives with specific groups containing oxygen and nitrogen as well as the various carbon-carbon bonds.

The *mass spectrometer* was used for two decades primarily as a research instrument before it began to be considered seriously as an analytical tool. During the 1940s the petroleum industry began to use the mass spectrometer in connection with the analysis of hydrocarbon mixtures. Although the quantitative interpretation of such mass spectrograms initially posed a formidable calculation problem, this instrument has proved to be highly successful in the petroleum industry, especially with the use of computerized techniques.

Emission spectroscopy has developed more rapidly than any other spectroscopic fields. Indeed, as early as 1920, it had reached a high level of usefulness. Practical procedures have been developed for the identification of metals and metalloids. The technique is sensitive to a few parts per million and thus is very useful for the identification of trace contaminants, as is often required in petroleum analysis.

And finally, in this note about spectroscopic methods, mention must be made of the use of *nuclear magnetic resonance spectroscopy* in petroleum analysis. The identification of hydrogen types (proton magnetic resonance) and carbon types (carbon magnetic resonance) must not pass unnoticed!

Analytical chemists usually classify chromatography as an instrumental method, but it is noted that it differs quite distinctly from the methods described above in objective and principle. Utilized for the most part in the separation of complex mixtures, it has only limited applicability to quantitative measurements where the complexity of petroleum is obvious.

Chemists have long known that many substances are adsorbed from gases and solutions onto the surface of solid materials. In fact, early experiments on the *adsorption* of petroleum constituents on adsorbents were reported at the First International Petroleum Congress held in Paris in 1900. Thus the importance of column adsorption was recognized in petroleum science as well as in chemical analysis in general. The method was soon put to work by petroleum chemists, as shown by descriptions of studies utilizing a column with ports at various levels from which samples might be withdrawn and studied to observe changes in boiling point, density, and viscosity.

Ion exchange materials, long known in the form of naturally occurring silicates, were used in the earliest types of regenerative water softeners. However, since 1930 chemists have had marked success in producing synthetic resins with ion exchange properties. Such resins are often used in ion exchange columns, which are highly effective in bringing about specific separations of petroleum constituents.

Gas chromatography, or vapor-phase chromatography, found ready applications in petroleum analysis since its introduction in 1952. The identification of the individual constituents of petroleum fractions was hailed worldwide. A last, some sense could be made of the composition of the complex system called petroleum! This technique 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.

There are many other analytical techniques that could be added to this catalogue of historical reminiscences, but that is not the object of this book.

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. Even though a wealth of data is available on petroleum from oilfields throughout the world, no entirely satisfactory system for classifying these oils has been developed.

Historically, physical properties such as boiling point, density (gravity), odor, and viscosity have been used to describe oils. However, because of the molecular complexity of petroleum, heavy oil, and bitumen, there is more to analysis, identification, and characterization than these four properties would indicate.

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 must be 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 oilfield separators, the temperatures and pressures of the separation plant, and the atmospheric temperature should be noted.

Elemental analyses of petroleum show that it contains mainly carbon and hydrogen. Nitrogen, oxygen, and sulfur (heteroelements) are present in smaller amounts and also trace elements such as vanadium, nickel, etc. 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/she 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 with 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; or
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 analysis of oilfield 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 a crude, 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.

Owing to the wide variation in the types of crude oil and to the fact that most companies have evolved their own assay methods, it has proved difficult to devise a rigid procedure to be followed in all cases, although there are considerable advantages to be gained if this were possible.

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.

Petroleum analysis involves not only determining the composition of the material under investigations 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.

A feedstock or product specification is therefore defined as 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 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 that was devised to measure performance of motor fuel. In other cases, the behavior must be determined indirectly from a series of test results.

Each test applied to petroleum and its products may have been justified by a high correlation with some important performance property, and it must also be recognized that many of the data from different tests are interrelated. The properties measured by many of the frequently used tests are far from independent of each other, and thus (interesting as this may be) there can be a considerable redundancy of information. For example, vapor pressure is closely related to front-end recovery in a distillation test, and flash point also bears some relationship to both these properties. Other examples are also evident and are presented throughout this text.

For the moment, another well-used example is the relationship of density (specific gravity or API gravity) to viscosity. It is up to the scientist and engineers involved to determine the tests that are necessary and the tests that are *redundant* (often defined in terms of *cost*).

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 using regression analysis is to examine at the specification as a whole and extract the essential features. This is termed *principal components analysis*.

Principal components analysis examines a set of data as points in *multidimensional space* (*n-dimensional*, corresponding to *n* original tests) and finds 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 it must be determined which 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.

It is in the interests of the refiner, the marketer, and the consumer to ensure that the specifications are efficient. When a refiner is manufacturing a product in compliance with a number of different marketing specifications, the manufacturing specification can be drafted in such a way as to ensure that these are all satisfied in the most efficient manner. In the case of particular marketing specifications, however, very little improvement can be achieved without the full cooperation of supplier and consumer.

Because of the difficulty of devising inspection tests that correlate sufficiently highly with the important performance properties of products, it is possible that there will be an increasing tendency for product quality to be specified in terms of suitably chosen indices that are not measured directly in the laboratory but are calculated from two or more measured properties.

Finally, the analytical methods used to describe conventional petroleum must be modified for the characterization of heavy oil and 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 heavy oil or bitumen or the potential product slates from each.

In fact, it is for the reason of behavior differences that research into test methods for heavy oil and bitumen is continuing (Wallace, 1988; Speight, 1999a,b). 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) 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 applying a wide variety of instrumental techniques to studies of the hydrocarbon composition of crude oils and their products (Chapter 10). Before this, hydrocarbon type analyses (percent paraffins, naphthenes, olefins, and aromatics) were derived from correlations based on physical data. The advent of instrumental techniques led to two major developments:

1. individual component analysis; and
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, by using 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 following 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.

From such knowledge of the chemical composition of petroleum distillates obtained using these instrumental techniques, and the information from the standard assays, the refiner is better able to predict and control crude oil operations and to assess the quality and performance of his/her products.

Thus petroleum analysis is a complex subject involving a variety of techniques, some of which are mentioned above. However, no single technique should supersede the other. Petroleum analysis is a complex discipline that needs a multidimensional approach, and an explanation of the data that are obtained needs adequate interpretation.

Understanding the methods and the data is the *raison d'être* of this book.

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CHAPTER

2

CHEMICAL COMPOSITION

2.1. INTRODUCTION

Petroleum is not a uniform material. In fact, its chemical and physical (fractional) composition can vary not only with the location and age of the oil field but also with the depth of the individual well (page 29). Indeed, two adjacent wells may produce petroleum with markedly different characteristics. On a molecular basis, petroleum is a complex mixture of hydrocarbons with small amounts of organic compounds containing sulfur, oxygen, and nitrogen, as well as compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper. The hydrocarbon content may be as high as 97% by weight in a lighter paraffinic crude oil or about 50% by weight in heavy crude oil and less than 30% by weight bitumen.

Nevertheless, crude oil (usually heavy crude oil) with as little as 50% by weight hydrocarbon components can still be classified with some degree of accuracy as a mixture of naturally occurring hydrocarbons. It will retain most of the essential characteristics of the hydrocarbons that will be reflected in the crude oil properties even though the nonhydrocarbon portion of the crude may actually consist of molecules containing one or perhaps two atoms of elements other than carbon and hydrogen (Gruse and Stevens, 1960; Speight, 1999, 2000 and references cited therein).

With the necessity of processing heavy oil, residua, and bitumen to obtain more gasoline and other liquid fuels, has come the recognition that knowledge of the constituents of these higher-boiling feedstocks is also of some importance to follow process chemistry and physics (Speight, 1999, 2000). Indeed, problems (such as phase separation and coking) encountered in processing the heavier feedstocks can be explained using this knowledge. Refining these materials is not just a matter of applying know-how derived from refining *conventional* crude oils but requires knowledge of the *chemical structure* and *chemical behavior* of these more complex constituents as they influence refining behavior.

Bitumen is extremely complex, and very little direct information can be obtained by distillation. It is not possible to isolate and identify its constituents using analytical techniques that rely on volatility. Other methods of identifying the chemical constituents must be employed, and these include a myriad of fractionation methods (Chapter 9) as well as methods designed to draw inferences

about the hydrocarbon skeletal structures and the nature of the heteroatomic functions (Chapter 8).

However, before any work is carried out in the laboratory, petroleum and petroleum products must go through a series of cleaning processes before shipping. Such processes might be the removal of dirt by membrane filters (ASTM D-2276, IP 216) or other processes that are specific to the nature of the crude oil as well as the recovery method used in the field. In the membrane filtration test, the dirt is retained by filtration of a sample through a cellulose membrane and is expressed as a weight per unit volume of the sample. Such a process may be applicable to field work, although desalting and dewatering processes are more amenable to field operations (see, for example, Speight, 1999).

Although more detail is given elsewhere (Chapter 9) on compositional studies, it is the purpose of this chapter to introduce the analytical chemist to the general chemical composition of petroleum, heavy oil, and bitumen, thereby *setting the stage* for what is to follow. In fact, as a result of this chapter the analyst should have some understanding of *the nature of the beast!*

2.2. ULTIMATE (ELEMENTAL) COMPOSITION

At one time, and perhaps even now depending on the crude oil, API gravity, sulfur content, and viscosity were the predominant data used to determine the quality of petroleum (Nelson, 1958; Gruse and Stevens, 1960; Speight, 1999, 2000 and references cited therein). As the quality of crude oils changed and the incorporation of hydroprocesses (hydrotreating and hydrocracking) into refinery scenarios became necessary to upgrade crude oils to products, the hydrogen content allowed refiners to estimate the amount of hydrogen need to convert crude oil to, for example, gasoline and diesel fuel. Thus, elemental analytical data are an important *first test* for petroleum. The atomic hydrogen-to-carbon ratio as well as the amount of sulfur (removal by conversion to H₂S) and nitrogen (removal by conversion to NH₃) became important data points. The amount of oxygen received lesser attention but is now also considered an important factor because of the potential for problems, such as corrosion of pipes, equipment, and reactors, caused by acidic compounds and their degradation products. Halogens from the associated brine were also effective corrosive agents and were detected by analytical techniques. At the same time, the amount of metals in feedstocks became an important issue because of catalyst degradation (Wojciechowski and Corma, 1986; Peterson and Bell, 1987; Gray, 1994).

Metal contents on the order of less than 100 ppm may seem insignificant to the general observer. However, when one considers that continuous operations and recycle operations can soon cause the metals on the catalyst to exceed 1000 ppm, leading to serious loss of catalyst activity, the issue becomes critical (Wojciechowski

and Corma, 1986; Peterson and Bell, 1987; Gray, 1994). Indeed, removal of sulfur and nitrogen as their respective hydrogen analogs did not completely eliminate their effect because both of the hydrogen analogs can result in catalyst deterioration and frequent replacement. The economics of catalyst production and purchase cannot tolerate frequent replenishment.

Therefore, as the refining industry of the twentieth century progressed and matured to include heavy feedstocks such as heavy oil and bitumen, the need for complete elemental analysis became obvious, indeed, conventional. Crude oil was not immune from such effects as nitrogen and metals can cause, even though the amounts of these materials in the feedstock were minimal. Concentration of sulfur compounds, nitrogen compounds, and metals in the residua (Speight, 2000) and the need to process the residua to liquid fuels (instead of the usual asphalt) added extra impetus to the need for complete analytical data.

Thus the complete elemental analysis of any feedstock became a necessary first step in determining the quality of the crude oil and the general behavior of its constituents. From the available data, it appears that the proportions of the elements in petroleum vary over fairly narrow limits (Speight, 1999, 2000 and references cited therein):

Carbon, 83.0–87.0%

Hydrogen, 10.0–14.0%

Nitrogen, 0.1–2.0%

Oxygen, 0.05–1.5%

Sulfur, 0.05–6.0%

Metals (Ni and V), <1000 ppm

despite the wide variation in physical properties from the lighter, more mobile crude oils at one extreme to the heavier asphaltic crude oils at the other extreme (see also Charbonnier et al., 1969; Draper et al., 1977). Indeed, when the many localized or regional variations in maturation conditions are assessed, it is perhaps surprising that the ultimate compositions are so similar. Perhaps this observation, more than any other observation, is indicative of the similarity in nature of the precursors from one site to another.

Thus it is not possible to classify petroleum because of the narrow range of carbon and hydrogen content in a manner analogous to the way in which coal is classified (Speight, 1994a). Other methods for petroleum classification must be sought, but these methods still require elemental analysis as well as the potential for producing hydrocarbon fuels.

The elemental analysis of tar sand bitumen has also been widely reported (Camp, 1976; Bunger et al., 1979; Meyer and Steele, 1981, Speight, 1999), but the data suffer from the disadvantages of being too sparsely scattered, and in many cases

identification of the source is too general (e.g., Athabasca tar sand, which covers several deposits) and is often not site specific. In addition, the analysis is quoted for bitumen that has been separated from the associated sand that may have been obtained by any one of several procedures and may therefore not be representative of the total bitumen on the sand. However, recent efforts have focused on a program to produce sound, reproducible data from samples for which the origin is carefully identified (Wallace et al., 1988). It is to be hoped that this program will continue, as it will provide a valuable database for tar sand and bitumen characterization.

Like conventional petroleum, from the data that are available, the elemental composition of tar sand bitumen is generally constant and falls into a narrow range (Speight, 1999, 2000 and references cited therein):

Carbon, $83.5 \pm 1.0\%$

Hydrogen, $10.5 \pm 0.5\%$

Nitrogen, $0.5 \pm 0.2\%$

Oxygen, $1.0 \pm 0.5\%$

Sulfur, $5.0 \pm 0.5\%$

Metals (Ni and V), $>1000 \text{ ppm}$

The major exception to these narrow limits is the oxygen content of bitumen, which can vary from as little as 0.2% to as high as 4.5%. This is not surprising because when oxygen is estimated by difference the analysis is subject to the accumulation of all of the errors in the other elemental data. In addition, bitumen is susceptible to aerial oxygen and the oxygen content is dependent on the sample history. More specifically, because of the amount of work done on this resource, the ultimate composition of the Alberta bitumen does not appear to be influenced by the proportion of bitumen in the oil sand or by the particle size of the oil sand minerals.

As already noted for the formation of *protopetroleum* (Chapter 1) and the subsequent maturation processes, when the many localized or regional variations in maturation conditions are assessed (Speight, 1999), it is perhaps surprising that the ultimate composition of one bitumen is similar to that of a different bitumen from another location.

Several generalities can be noted from the ultimate composition that might be used to give general indications of how the material might behave during processing (AOSTRA, 1984; Wallace, 1988). For example, the atomic hydrogen-carbon ratio is generally related to bitumen viscosity insofar as trends can be shown graphically and hence can be an indicator of the required supplementary heat energy for thermal extraction processes. The hydrogen-carbon atomic ratio may also be shown to bear a relationship to the API gravity and to the pour point. However, these trends are not too specific and may, because of the scarcity of data, be only fortuitous.

There is a relationship of pour point to API gravity for specific families of heavy oil and bitumen that allows prediction of oil mobility or immobility in the reservoir (Chapter 5). However, it is certain that the atomic hydrogen-carbon ratio is related to the hydrogen requirements during processing. The higher the hydrogen-carbon ratio of bitumen, the higher is its value as refinery feedstock because of the lower hydrogen requirements.

The nitrogen content of petroleum and heavy oil is usually less than 1.0% by weight and often less than 0.5% by weight, but the nitrogen content of tar sand bitumen can be as high as 1.3% by weight. The nitrogen complicates the refining process by poisoning the catalysts used (Wojciechowski and Corma, 1986; Peterson and Bell, 1987; Gray, 1994). Elements related to nitrogen content are sulfur content, hydrogen content, hydrogen-carbon ratio, and distillation profile.

The occurrence of sulfur in petroleum, heavy oil, and bitumen as organic or elemental sulfur or in produced gas as compounds with oxygen and hydrogen is an expensive nuisance and therefore, like the nitrogen content, must be known accurately. The sulfur must be removed from the bitumen at some point in the upgrading and refining process.

2.3. CHEMICAL COMPOSITION

The chemical composition of the volatile fractions of petroleum has been covered in several texts (Speight, 1999 and references cited therein). However, the chemical composition of the heavier feedstocks is, despite the large volume of work performed in this area, largely speculative. In fact, the precise chemical composition of petroleum can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells may even produce petroleum with very different characteristics. However, general deductions about the nature of the chemical constituents can be made.

In very general terms (and as observed from elemental analyses), petroleum, heavy oil, bitumen, and residua are *molecular mixtures* of: (a) hydrocarbons, (b) nitrogen compounds, (c) oxygen compounds, (d) sulfur compounds, and (e) metallic constituents. However, this general definition is not adequate to describe the composition of petroleum et al. as it relates to the behavior of these feedstocks. Indeed, the consideration of the atomic hydrogen-carbon ratio, sulfur content, and API gravity are no longer sufficiently adequate to the task of determining refining behavior.

Feedstock behavior during refining is better addressed through consideration of the molecular make-up of the feedstock (perhaps, by analogy, just as genetic make-up dictates human behavior). The occurrence of amphoteric species (i.e., compounds having a mixed acid/base nature) is not addressed, nor is the phenomenon of molecular size or the occurrence of specific functional types

(ASTM F-1186) that can play a major role in the interactions between the constituents of a feedstock. All of these items are important in determining feedstock behavior during refining operations.

The hydrocarbon content of petroleum may be as high as 97% by weight (for example, in the lighter paraffinic crude oils). It is, nevertheless, the nonhydrocarbon (sulfur, oxygen, nitrogen, and metal) constituents that play a large part in determining the processability of the crude oil (Rossini et al., 1953; Brooks et al., 1954; Lochte and Littmann, 1955; Schwartz and Brasseaux, 1958; Brandenburg and Latham, 1968; Rall et al., 1972). But there is more to the composition of petroleum than the hydrocarbon content. The inclusion of organic compounds of sulfur, nitrogen, and oxygen serves only to present crude oils as even more complex mixtures, and the appearance of appreciable amounts of these nonhydrocarbon compounds causes some concern in the refining of crude oils. Even though the concentration of nonhydrocarbon constituents (i.e., those organic compounds containing one or more sulfur, oxygen, or nitrogen atoms) in certain fractions may be quite small, they tend to concentrate in the higher-boiling fractions of petroleum. Indeed, their influence on the processability of the petroleum is important irrespective of their molecular size and the fraction in which they occur.

The presence of traces of nonhydrocarbon compounds can impart objectionable characteristics to finished products, leading to discoloration and/or lack of stability during storage. On the other hand, catalyst poisoning and corrosion are the most noticeable effects during refining sequences when these compounds are present (Wojciechowski and Corma, 1986; Peterson and Bell, 1987; Gray, 1994). It is therefore not surprising that considerable attention must be given to the nonhydrocarbon constituents of petroleum, because the trend in the refining industry, of late, has been to process more heavy crude oil as well as residua that contain substantial proportions of these nonhydrocarbon materials (Gray, 1994; Speight, 2000).

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

2.3.1. Hydrocarbon Components

The study of the individual hydrocarbon constituents in petroleum began in the 1850s when alkylbenzenes were reported in a petroleum from Burma. Later, methylcyclopentane was isolated from a Caucasian petroleum, followed by the isolation of paraffin hydrocarbons from various petroleum fractions. Distillation techniques (Chapter 5) were also employed in some of this early work, and the separation of cyclohexane by crystallization of a distillate fraction into which it had been concentrated is an example of what could be accomplished at that early date.

Nevertheless, the isolation of pure compounds from petroleum is an exceedingly difficult task, even though specific tests are available for the detection of hydrocarbons in petroleum (ASTM, 1998). Hydrocarbon constituents in lower-boiling fractions can be detected using methods based on, for example, gas chromatography (ASTM D-2360, ASTM D-2597, ASTM D-2600, ASTM D-4626, ASTM D-5134) or by mass spectrometry (ASTM D-2425, ASTM D-2786, ASTM D-2789) (Chapter 4), but the overwhelming complexity of the hydrocarbon constituents of the higher-molecular-weight fractions as well as the presence of compounds of sulfur, oxygen, and nitrogen are the main causes for the difficulties encountered.

It is difficult on the basis of the data obtained from synthesized hydrocarbons to determine the identity or even the similarity of the synthetic hydrocarbons to those that constitute many of the higher-boiling fractions of petroleum. Nevertheless, it has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups. Olefinic groups are not usually found in crude oils but can be determined (ASTM D-1159; ASTM D-1319; ASTM E-234), and acetylenic hydrocarbons are very rare indeed. It is therefore convenient to divide the hydrocarbon components of petroleum into the following three classes:

1. *Paraffins*, which are saturated hydrocarbons with straight or branched chains, but without any ring structure.
2. *Naphthenes*, which are saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as *alicyclic hydrocarbons*).
3. *Aromatics*, which are hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, which may be linked up with (substituted) naphthene rings and/or paraffinic side chains.

The general changes in the composition of petroleum fractions with boiling point or range are significant. However, most of the published work has focused on particular boiling fractions (for example, the fraction boiling up to vacuum residua)

of petroleum composition, and an all-encompassing expression of variation of petroleum composition in terms of its variation with both boiling point and crude origin is only now starting to become available (Altgelt and Boduszynski, 1994; Speight, 1999).

It is the goal of this chapter to present a general picture of the constituents of petroleum and the manner in which the chemical types vary with boiling point.

2.3.1.1. Paraffin Hydrocarbons

The proportion of paraffins in crude oils varies with the type of crude, but within any one crude oil, the proportion of paraffinic hydrocarbons usually decreases with increasing molecular weight or boiling point (Fig. 2.1). In the gasoline range, for instance, paraffin contents as high as 80% have been noted, whereas in the lubricating oil range a 30% paraffin content is exceptionally high. In fact, many oils yield lubricating fractions that are totally devoid of paraffins. It is now known that such trends of molecular composition continue into the (nonvolatile) resin and asphaltene constituents based on the concept that petroleum is a continuum (Chapter 14) and that specific compound types exist through the whole crude

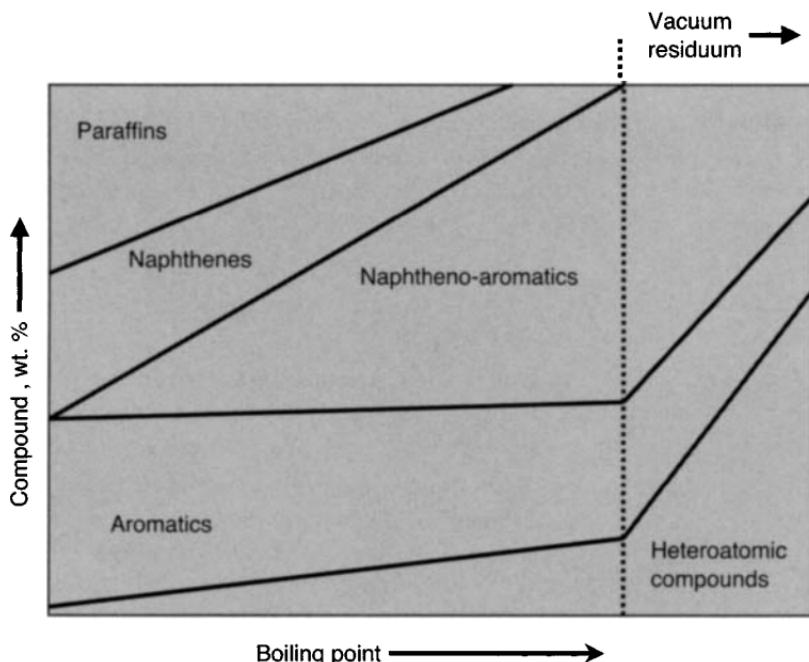


Figure 2.1. Distribution of various compound types throughout petroleum.

oil. The difference, of course, is found in the molecular weight of the individual compound types (Speight, 1999, 2000).

The relationship between the various hydrocarbon constituents of crude oils is one of hydrogen addition or hydrogen loss (Speight, 1999), and there is no reason to deny the occurrence of these interconversion schemes during the formation, maturation, and *in situ* alteration of petroleum. Indeed, a scheme of this type lends even more credence to the complexity of petroleum within the hydrocarbon series alone.

The abundance of the different members of the same homologous series varies considerably in absolute and relative values. However, in any particular crude oil or crude oil fraction, there may be a small number of constituents forming the greater part of the fraction, and these have been referred to as the *predominant constituents* (Rossini and Mair 1959; Bestougeff, 1961). This generality may also apply to other constituents and is very dependent on the nature of the source material as well as the relative amounts of the individual source materials prevailing during maturation conditions (Chapter 1).

Normal paraffin hydrocarbons (n-paraffins, straight-chain paraffins) occur in varying proportions in most crude oils. In fact, paraffinic petroleum may contain up to 20–50% by weight *n*-paraffins in the gas oil fraction. One particular gas oil (boiling range 150–350°C, 300–660°F) contained every possible normal paraffin that could be present in this fraction. Furthermore, all the normal paraffins up to and beyond *n*-dodecane (12 carbon atoms) have been isolated from crude oil. However, naphthenic or asphaltic crude oils sometimes contain only very small amounts of normal paraffins, as illustrated by the isolation of less than 1% of paraffins from Borneo crude oil.

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

As the molecular weight (or boiling point) of the petroleum fraction increases, there is a concomitant decrease in the amount of free paraffins in the fraction. In certain types of crude oil, there may be no paraffins at all in the vacuum gas oil fraction. For example, in the paraffinic crude oils, free paraffins will separate as a part of the asphaltene fraction but in the naphthenic crude oils, free paraffins are not expected in the gas oil and asphaltene fractions.

The vestiges of paraffins in the asphaltene fractions occur as alkyl side chains on aromatic and naphthenic systems, and these alkyl chains can contain forty or more carbon atoms (Chapter 14).

On a boiling range basis, the low-boiling naphtha fraction (<150°C, <300°F) consists mainly of paraffins (Speight, 1999). Any ring compounds are restricted to alkylcyclohexanes and alkylcyclopentanes and to alkylbenzenes. The sulfur content varies from a few parts per million to several hundreds of parts per million. The nitrogen content is so low that it is rarely measured.

2.3.1.2. *Cycloparaffin Hydrocarbons (Naphthenes)*

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

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

The principal structural variation of naphthenes is in the number of rings present in the molecule. The mono- and bicyclic naphthenes are generally the major types of cycloparaffins in the lower-boiling fractions of petroleum, with boiling point or molecular weight increased by the presence of alkyl chains. The higher-boiling-point fractions, such as the lubricating oils, may contain two to six rings per molecule.

The higher-boiling naphtha fractions (150–200°C, 300–390°F) are mainly aliphatic, but they contain lesser amounts of paraffins at the expense of higher amounts of mono- and dinaphthenes. The aromatics may account for as much as 20 wt% and consist of paraffin moieties in alkylbenzenes. The sulfur content ranges from a few hundred parts per million to as high as 2% by weight. The nitrogen content is usually <1 ppm.

The kerosene fraction (200–260°C, 400–500°F) typically contains about 70–80% by weight saturates and 20–30% by weight aromatics. The saturated components are considerably more naphthenic than those in the lower-boiling fractions, but this is dependent on the crude oil. Hydrocarbons with one or two naphthenic and aromatic rings may be present. The sulfur content may vary from 0.05 to 3.0% by weight, mainly in the form of sulfides, in acyclic as well as cyclic alkanes, and of alkylthiophenes and benzothiophenes. The nitrogen content is typically a few parts per million, but may be higher.

As the molecular weight (or boiling point) of the petroleum fraction increases to higher ranges, there is a concomitant increase in the amount of cycloparaffinic (naphthenic) species in the fraction. In the asphaltic (naphthenic) crude oils, the gas oil fraction can contain considerable amounts of naphthenic ring systems that increase even more in consideration of the molecular types in the asphaltenes. However, as the molecular weight of the fraction increases, the occurrence of condensed naphthene ring systems and alkyl-substituted naphthene ring systems increases. There is also the premise that the naphthene ring systems carry alkyl chains that are generally longer than the alkyl substituents carried by aromatic systems. This can be reflected on hypothetical structures for the asphaltene constituents (Chapter 14).

In the asphaltene fraction, free condensed naphthenic ring systems may occur but general observations favor the occurrence of combined aromatic-naphthenic systems that are variously substituted by alkyl systems. There is also general evidence that the aromatic systems are responsible for the polarity of the asphaltene constituents. The heteroatoms are favored to occur on or within the aromatic (pseudoaromatic) systems (Chapter 14).

2.3.1.3. *Aromatic Hydrocarbons*

The occurrence of identifiable aromatic systems in nature is a reality, and the occurrence of monocyclic and polycyclic aromatic systems in natural product chemicals is well documented (Sakarnen and Ludwig, 1971; Durand, 1980; Weiss and Edwards, 1980). However, one source of aromatic systems that is often ignored is petroleum (Eglinton and Murphy, 1969; Tissot and Welte, 1978; Speight, 1981; Brooks and Welte, 1984). Therefore, attempts to identify such systems in the nonvolatile constituents of petroleum should be an integral part of the repertoire of the petroleum chemist as well as the domain of the natural product chemist.

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

There is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight. However, aromatic hydrocarbons without the

accompanying naphthalene rings or alkyl-substituted derivatives seem to be present in appreciable amounts only in the lower petroleum fractions. Thus, the limitations of instrumentation notwithstanding, it is not surprising that spectrographic identification of such compounds has been concerned with these low-boiling aromatics.

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

In summation, all hydrocarbon compounds that have aromatic rings, in addition to the presence of alkyl chains and naphthenic rings within the same molecule, are classified as aromatic compounds. Many separation procedures that have been applied to petroleum (Chapter 10) result in the isolation of a compound as an *aromatic* even if there is only one such ring (i.e., 6 carbon atoms) that is substituted by many more than six nonaromatic carbon atoms.

Although not specifically discussed here, a variety of pericondensed polycyclic aromatic hydrocarbons such as methylchrysene, methyl- and dimethylperlylenes, and benzofluorenes have been identified in crude oil. Chrysene and benzofluorene homologues seem to predominate over those of pyrene.

It should also be emphasized that in the higher-boiling-point petroleum fractions, many polycyclic structures occur in naphthenoaromatic systems. The naphthenoaromatic hydrocarbons, together with the naphthenic hydrocarbon series, form the major content of higher-boiling-point petroleum fractions. Usually, the different naphthenoaromatic components are classified according to the number of aromatic rings in their molecules. The first to be distinguished is the series with an equal number of aromatic and naphthenic rings. The first members of the bicyclic series C₉–C₁₁ are the simplest, such as the 1-methyl-, 2-methyl, and 4-methylindanes and 2-methyl- and 6-methyltetralins. Tetralin and methyl-, dimethyl-, methylethyl-, and tetramethyltetralin have been found in several crude oils, particularly in the heavier, naphthenic crude oils.

It is interesting that the distribution of the chains between aromatic and naphthenic rings within the same molecules follows a particular pattern that may also be evident in the single-ring constituents. The short chains (methyl and ethyl) appear to be characteristic substituents of the aromatic portion of the molecule, whereas a limited number (1 or 2) of longer chains may be attached to the cycloparaffin rings. The total number of chains, which is in general four to six, as well as their length, increases according to the molecular weight of the naphthenoaromatic compounds.

Atmospheric gas oils (260–345°C, 500–650°F) may have considerable amounts of aromatics and detectable amounts of polar constituents (Altgelt and Boduszynski, 1994; Speight, 1999 and references cited therein). Besides mono- and dinaphthalenes, alkylbenzenes, and alkynaphthalenes, the atmospheric gas oil fraction may contain small amounts of higher-ring-number naphthalenes and aromatics. Sulfur contents are typically around 1.5–3.0% by weight but may occasionally reach 4.5% by weight. Besides dialkyl-, alkylaryl-, and arylaryl sulfides and the alkylthiophenes and benzothiophenes, there may now also be some dibenzothiophene derivatives. Nitrogen content is usually a few hundreds of parts per million, but it may go up to 1500 ppm for some crude oils.

Of special interest in the present context are the aromatic systems that occur in the nonvolatile asphaltene fraction (Speight, 1994b). These polycyclic aromatic systems are complex molecules that fall into a molecular weight and boiling range where very little is known about model compounds (Chapter 15). There has not been much success in determining the nature of such systems in the higher-boiling constituents of petroleum, i.e., the residua or nonvolatile constituents. In fact, it has been generally assumed that as the boiling point of a petroleum fraction increases, so does the number of condensed rings in a polycyclic aromatic system. To some extent this is true, but the simplicities of such assumptions cause an omission of other important structural constituents of the petroleum matrix, the alkyl substituents, the heteroatoms, and any polycyclic systems that are linked by alkyl chains or by heteroatoms.

The active principle is that petroleum is a continuum (Corbett and Petrossi, 1978; Long, 1979, 1981) (Chapter 14) and has natural product origins (Speight, 1981, 1994b, 1999) (Chapter 1). As such, it might be anticipated that there is a continuum of aromatic systems throughout petroleum that might differ from volatile to nonvolatile fractions but that, in fact, are based on natural product systems. It might also be argued that substitution patterns of the aromatic nucleus that are identified in the volatile fractions, or in any natural product counterparts, also apply to the nonvolatile fractions.

The application of thermal techniques to study the nature of the volatile thermal fragments from petroleum asphaltenes has produced some interesting data relating to the nature of the aromatic systems in crude oil (Ritchie et al., 1979a, 1979b; Schucker and Keweshan, 1980; Gallegos, 1981; Raul, 1982; Speight, 1999 and references cited therein). These thermal techniques have produced strong evidence for the presence of small (1–4 ring) aromatic systems (Speight and Pancirov, 1984; Speight, 1987). There was a preponderance of single-ring (cycloparaffin and alkylbenzene) species as well as the domination of saturated material over aromatic material.

Further studies using pyrolysis/gas chromatography/mass spectrometry (Speight and Pancirov, 1984) showed that different fractions of an asphaltene would produce the same type of polycyclic aromatic systems in the volatile matter, but the

distribution was not constant (Chapter 11). It was also possible to compute the hydrocarbon distribution from which, a noteworthy point here, there is preponderance of single ring (cycloparaffin and alkylbenzene) species as well as the domination of saturated material over aromatic material. The emphasis on low-molecular-weight material in the volatile products is to be anticipated on the basis that more complex systems remain as nonvolatile material and, in fact, are converted to coke.

One other point worthy of note is that, at that time, the pyrolysis/gas chromatography/mass spectrometry program did not accommodate nitrogen and oxygen species, whether or not they be associated with aromatic systems. This matter was resolved, in part, not only by the concentration of nitrogen and oxygen in the nonvolatile material (coke) but also by the overall low proportions of these heteroatoms originally present in the asphaltenes (Speight and Pancirov, 1984; Speight, 1994b). The major drawback to the use of the pyrolysis/gas chromatography/mass spectrometry method to studying aromatic systems in asphaltenes is the amount of material that remains as a nonvolatile residue.

Of all of the methods applied to determining the types of aromatic systems in petroleum asphaltenes, one with considerable potential, but given the least attention, is ultraviolet spectroscopy (Friedel and Orchin, 1951; Braude and Nachod, 1955; Rao, 1961; Jaffe and Orchin, 1966; Lee et al., 1981; Bjorseth, 1983).

Typically, the ultraviolet spectrum of an asphaltene fraction shows two major regions with very little fine structure. Interpretation of such a spectrum can only be made in general terms (Friedel, 1959; Boyd and Montgomery, 1963; Posadov et al., 1977). However, the technique can add valuable information about the degree of condensation of polycyclic aromatic ring systems through the auspices of high-performance liquid chromatography (*HPLC*) (Lee et al., 1981; Bjorseth, 1983; Monin and Pelet, 1983; Felix et al., 1985; Killops and Readman, 1985; Speight, 1986). Indeed, when this approach is taken the technique not only confirms the complex nature of the asphaltene fraction but also allows further detailed identifications to be made of the individual functional constituents of asphaltenes. An asphaltene fraction produces a multicomponent chromatogram (Chapter 10) but subfractions produce a less complex and much narrower chromatograph that may even approximate a single peak that may prove much easier to monitor by the ultraviolet detector.

These data provide strong indications of the ring-size distribution of the polycyclic aromatic systems in petroleum asphaltenes. For example, from an examination of various functional subfractions, it was shown that amphoteric species and basic nitrogen species contain polycyclic aromatic systems having two to six rings per system. On the other hand, acid subfractions (phenolic and/or carboxylic functions) and neutral polar subfractions (amide and/or imino functions) contain few if any polycyclic aromatic systems having more than three rings per system (Chapter 10).

In all cases, the evidence favored the preponderance of the smaller (1–4) ring systems (Speight, 1986). But perhaps what is more important about these investigations is that the data show that asphaltenes are a complex mixture of compound types, which confirms fractionation studies, and cannot be represented by any particular formula that is construed to be *average*. Therefore, the concept of a large polycyclic aromatic ring system as the central feature of asphaltene molecules must be abandoned.

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

2.3.1.4. *Unsaturated Hydrocarbons*

The presence of olefins ($R.CH=CH.R^1$) in petroleum has been under dispute for many years because there are investigators who claim that olefins are actually present; in fact, these claims usually refer to distilled fractions, and it is very difficult to entirely avoid cracking during the distillation process. Although there may be fragmentary evidence for the presence of olefins (albeit in very small amounts) in petroleum, it is perhaps reasonable to assume that olefins are present in crude oils in only a few special cases. The presence of dienes ($R.CH=CH-CH=R^1$) and acetylenes ($RC\equiv C.R^1$) is considered to be extremely unlikely.

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

2.3.2. *Nonhydrocarbon Components*

The previous sections present some indication of the types and nomenclature of the organic hydrocarbons that occur in various crude oils. Thus it is not surprising that petroleum that contains only hydrocarbons is, in fact, an extremely complex mixture. The phenomenal increase in the number of possible isomers for the higher hydrocarbons makes it very difficult, if not impossible in most cases, to isolate individual members of any one series having more than, say, 12 carbon atoms.

Inclusion of organic compounds of nitrogen, oxygen, and sulfur serves only to present crude oil as an even more complex mixture than was originally conceived (Altgelt and Boduszynski, 1994; Speight, 1999, 2000). Nevertheless, considerable progress has been made in the isolation and/or identification of the lower-molecular-weight hydrocarbons, as well as accurate estimations of the overall proportions of the hydrocarbon types present in various crude oils. Indeed, it has been established that, as the boiling point of the petroleum fraction increases, not only the number of the constituents but also the molecular complexity of the constituents increases (Fig. 2.1).

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

As the boiling range of the petroleum fractions increases, the concentration of saturates decreases but the content of ring compounds (naphthenic compounds and aromatic compounds) increases. Most aromatics are alkylbenzenes and naphthalenes, some of which may contain one or several naphthenic rings. In the middle distillates and the lower-boiling fractions, the five major sulfur compound classes (viz., thiols, sulfides, disulfides, sulfoxides, and thiophene derivatives, mainly benzothiophenes) occur. Nitrogen compounds are mostly pyrroles, indoles, pyridines, and quinolines (Altgelt and Boduszynski, 1994; Speight, 1999, 2000). Among the oxygen compounds, aliphatic carboxylic acids, aliphatic esters, ketones and other carbonyl derivatives as a group, dibenzofurans, and phenols are also abundant in the atmospheric gas oil fraction. The concentration of polar constituents in fractions boiling below 345°C (650°F) usually does not exceed 5–10% by weight.

Although their concentration in certain fractions may be quite small, their influence is important. For example, the decomposition of inorganic salts suspended in the crude can cause serious breakdowns in refinery operations; the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. The presence of organic acid components, such as mercaptans and acids, can also promote metallic corrosion. In catalytic operations, passivation and/or poisoning of the catalyst can be caused by deposition of traces of metals (vanadium and nickel) or by chemisorption of nitrogen-containing compounds on the catalyst, thus necessitating the frequent regeneration of the catalyst or its expensive replacement (Wojciechowski and Corma, 1986; Peterson and Bell, 1987; Gray, 1994; Speight, 2000).

The presence of traces of nonhydrocarbons may impart objectionable characteristics to finished products, such as discoloration, lack of stability on storage, or a reduction in the effectiveness of organic lead antiknock additives. It is thus obvious that a more extensive knowledge of these compounds and of their characteristics could result in improved refining methods and even in finished products of better quality. The nonhydrocarbon compounds, particularly the porphyrins and related compounds, are also of fundamental interest in the elucidation of the origin and nature of crude oils. Furthermore, a knowledge of their surface-active characteristics is of help in understanding problems related to the migration of oil from the source rocks to the actual reservoirs.

With the aromatics and polar constituents, the likelihood of molecules having more than one heteroatom further complicates the structural types and can certainly

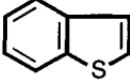
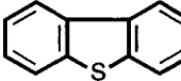
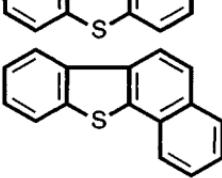
complicate the analysis for molecular types. Most aromatic and polar molecules in the heavy gas oil range contain one to three aromatic rings, predominantly with naphthenic rings. Compounds with four and more aromatic rings are present at much lower concentrations.

In addition, heterocompound types with more aromatic rings may be found, e.g., benzonaphtho- and dinaphthothiophenes, benzo- and naphthoquinolines, aza- and diaza derivatives. Compounds with two and three heteroatoms such as amides, aza-amides, sulfoxides, carboxylic acids, and hydroxycarboxylic acids also occur (Altgelt and Boduszynski, 1994; Speight 1999, 2000 and references cited therein).

2.3.2.1. *Sulfur Compounds*

Sulfur compounds are among the most important heteroatomic constituents of petroleum, and, although there are many varieties of sulfur compounds (Table 2.1), the prevailing conditions during the formation, maturation, and even

Table 2.1. Types and Nomenclature of Organic Sulfur Compounds

RSH	Thiols (Mercaptans)
RSR'	Sulfides
	Cyclic Sulfides
RSSR'	Disulfides
	Thiophene
	Benzothiophene
	Dibenzothiophene
	Naphthobenzothiophene
	

in situ alteration may dictate that only preferred types exist in any particular crude oil. Nevertheless, sulfur compounds of one type or another are present in all crude oils; in general, the higher the density of the crude oil (or the lower the API gravity of the crude oil), the higher the sulfur content (Speight, 1999, 2000). The total sulfur in the crude can vary from 0.04% by weight for a light crude oil to about 5.0% for bitumen. However, the sulfur content of crude oils produced from broad geographic regions varies with time, depending on the composition of newly discovered fields, particularly those in different geological environments.

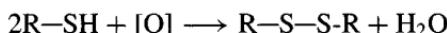
The presence of sulfur compounds in finished petroleum products often produces harmful effects. For example, in gasoline, sulfur compounds promote corrosion of engine parts, especially under winter conditions, when water containing sulfur dioxide from the combustion may accumulate in the crankcase. In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

The distribution of sulfur in the various fractions of crude oils has been studied many times, beginning in 1891. Although it is generally true that the proportion of sulfur increases with the boiling point during distillation (Speight, 1999, 2000), the middle fractions may actually contain more sulfur than higher-boiling fractions as a result of decomposition of the higher-molecular-weight compounds during the distillation. A high sulfur content is generally considered harmful in most petroleum products, and the removal of sulfur compounds or their conversion to less deleterious types is an important part of refinery practice. The distribution of the various types of sulfur compounds varies markedly among crude oils of diverse origin, but fortunately some of the sulfur compounds in petroleum undergo thermal reactions at relatively low temperatures. If elemental sulfur is present in the oil, a reaction, with the evolution of hydrogen sulfide, begins at about 150°C (300°F) and is very rapid at 220°C (430°F), but organically bound sulfur compounds do not yield hydrogen sulfide until higher temperatures are reached. Hydrogen sulfide is, however, a common constituent of many crude oils, and some crude oils with >1% sulfur are often accompanied by a gas having substantial proportions of hydrogen sulfide.

Several tests are used to determine the amount of sulfur in petroleum and its products, but the actual determination of sulfur in functional groups is more

difficult. Nevertheless, the identification of sulfur-containing constituents of crude oils has been the subject of many investigations with the result that many of the sulfur compound types that occur in crude oils are now known (Thompson et al., 1976). These vary from the simple thiols ($R-SH$) to the simple sulfides ($R-S-R$) and the polycyclic sulfides, such as compounds with two condensed rings (Table 2.1).

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



At the functional group level, the sulfur compounds reported in crude and fractions include thiols (mercaptans), sulfides, disulfides, and thiophenes (Robbins, 2000). Generally, however, the bulk of the sulfur in whole crude occurs as sulfides and thiophenes. The distinction between sulfides and thiophenes is of practical interest because of their wide differences in reactivity. For example, the thiophenes, unlike the sulfides, are noncorrosive and are the most difficult sulfur types to remove from fuels.

The measurement of the distribution thiophene/sulfide sulfur types is not as straightforward as elemental analysis. Generally, the sulfur in a crude oil is 67% thiophene and 33% sulfide (thioether). This is based on experience in comparing total sulfur with some of the common methods used for measuring the sulfide sulfur. The latter has been determined indirectly by titration, complexation, and oxidation-Fourier transform infrared spectroscopy (FTIR) on whole oils and distillates and directly by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectroscopy (XANES) measurements on residua and asphaltenes.

The indirect methods typically involve *selective* reaction, but few have been validated independently or compared with one another. Measurements of sulfides by sulfur analyses after separation methods likewise fail to report sulfur recoveries, provide material balances on real samples, or otherwise demonstrate selectivity or accuracy. The direct techniques measure both sulfur types by deconvolution of sulfide and thiophene overlapping peaks in the spectra. Overall, the results reported by the various techniques show a much wider range of sulfide sulfur than implied by the above generalization (Robbins, 2000). The proportion of sulfide sulfur in petroleum and distillates varies from <10 to >60% by weight of the total sulfur depending on the boiling range, source of the petroleum, and maturation.

The uncertainty in the efficiency of sulfur-type separations has limited the characterization of molecular species despite the introduction of a number of

sophisticated measurement techniques. Reactivity differences are recognized between the various types of sulfur, but few contributing structural features have been identified or quantified. Differences in corrosivity, thermal stability, and oxidative inhibition have been attributed to variation in sulfide structure. Differences in process resistance by thiophenes are attributed to steric effects. Some techniques have been developed for molecular structural characterization, but these provide limited data on narrow areas of interest.

For example, geochemical studies have identified several structural families in crude oils and source materials (see, e.g., Fig. 2.1). These include the homologous series of C₁₇–C₃₁ bicyclic, C₂₂–C₄₀ tetracyclic, and even C₃₀–C₃₅ hexacyclic terpenoid sulfides in the heavy oils. Structure of the most abundant member of the bicyclic series was proven by hydrogenolysis/mass spectrometry of the resulting hydrocarbon skeleton and by synthesis. The C₈–C₃₀ dialkylthianes and dialkylthiolanes were characterized with similar techniques after separation from the terpenoid sulfides by thiourea adduction. Because higher homologues have been reported in extracts of recent sediments, these linear monocyclic sulfides serve as biomarkers for immature crude oils.

These analyses, however, intentionally reject the bulk of the sulfur compounds to focus on the biomarker structures. The isolation procedures include multiple reactions and chromatographic separation. Although excellent recovery (98%) is reported for the selective oxidation of model compounds, the sulfur balances for real samples are difficult to estimate. Thus, although the characterization provides a geochemist with biomarker data, it gives an incomplete characterization of sulfides that can impact processing and products.

For more complete characterization of sulfur types, specifically sulfide sulfur, the first challenge is to demonstrate an isolation technique that is both selective and quantitative. That is, the sulfur balance (total sulfur and proportion of sulfide sulfur) measurements on each fraction are needed for each step of an isolation scheme. Once the selective isolation of sulfides has been verified, the methods of measuring molecular structure (e.g., ring number, molecular weight, sulfur bonding) can be applied to rationalize differences.

Another example of improved sulfur-type separation can be found in the thiophenes. However, after advanced hydroprocessing, trace refractory sulfur compounds are found in diesel and gasoline distillates by gas chromatography. Dibenzothiophene and alkylated homologues are a major contributor to sulfur in distillate feeds. After conventional processing, the residual sulfur is distributed across numerous sterically hindered dibenzothiophene isomers, such as 4,6 dimethyl dibenzothiophene. The hindered dibenzothiophenes account for less than half the GC/SCD peaks, with the remainder being distributed across the numerous *unknown molecular species* at the parts-per-million level. The challenge in the characterization of these thiophene *unknowns* is the development of a sulfur-selective isolation that would allow characterization of the molecular structure.

Many methods have been proposed for the isolation of dibenzothiophene homologues in petroleum samples. Most begin with the separation of the aromatics (i.e., alumina or silica gel) followed by some type of *sulfur-selective* isolation of the thiophene species. Two approaches are commonly suggested for separation of thiophenes from the aromatics.

The first approach uses ligand exchange with a supported metal. Separations using silver (Ag^+), copper (Cu^{2+}), and mercury (Hg^{2+}) as the ligand are limited to the separation of thiophenes and aromatics with same number of aromatic rings.

If a wide group of aromatics is treated with these ligands, the thiophenes overlap with higher aromatics, i.e., benzothiophene (2-ring sulfur) elutes with the phenanthrenes (3-ring aromatics). Palladium (Pd^{2+}) is more retentive and requires stronger solvents for elution. If the solvent is too strong, the palladium-thiophene complex is eluted and it must be treated with an amine treatment to release the thiophene species.

The second approach uses a combination of oxidation, chromatographic separation, reduction, and a second chromatographic step. In such an approach, the effect of steric hindrance on each step must be given consideration; otherwise, the selectivity and completeness of each step is in serious doubt. Mass recovery and model sulfur-recovery in single steps have been reported for some versions. But the overall sulfur-recovery for oxidative separation of thiophenes is lacking.

The separation of thiophenes from the fuel distillates is challenging because some of the structures to be isolated are indeed unknown and the remainder are sterically hindered. The development of a suitable sulfur-selective separation will require sulfur recovery data for each step of an isolation scheme. If the product has been hydroprocessed, the sulfur species can be assumed to be thiophene. Once isolated, the thiophenes can be characterized using existing methods for measuring molecular structure (e.g., ring number, molecular weight, sulfur bonding). The value of the new sophisticated measurement techniques can be improved with the development of better separations.

Although sulfur is the most important (certainly the most abundant) heteroatom (i.e., nonhydrocarbon) present in petroleum with respect to the current context, other nonhydrocarbon atoms can exert a substantial influence not only on the nature and properties of the products but also on the nature and efficiency of the process. Such atoms are nitrogen, oxygen, and metals, and because of their influence on the process, some discussion of each is warranted here.

2.3.2.2. *Oxygen Compounds*

The analysis for oxygen in petroleum has taken an arduous route. Initially, as for coal, oxygen was determined by difference after the amounts of all of the other elements had been determined. The assumption, was, of course, that each

Table 2.2. Types and Nomenclature of Organic Oxygen Compounds

Alcohols	
Methyl alcohol	CH ₃ OH
Phenol	C ₆ H ₅ OH
Ethers	
Dimethyl ether	CH ₃ OCH ₃
Diphenyl ether	C ₆ H ₅ OC ₆ H ₅
Carboxylic acids	
Acetic acid	CH ₃ CO ₂ H
Benzoic acid	C ₆ H ₅ CO ₂ H
Esters	
Ethyl acetate	CH ₃ CO ₂ CH ₂ CH ₃
Ketones	
Acetone	CH ₃ COCH ₃
Furans	
Furan	CH=CHOCH=CH

particular method was accurate and that the difference between the sum total of the other elemental analyses and 100% was the true value of the amount of oxygen. Unfortunately, this was not always true. However, the oxygen content of the light crude oils was often so insignificant as to be ignored by investigators. With the appearance of heavier feedstocks in refineries, oxygen cannot be ignored, so several methods have been developed for accurate analysis of oxygen in feedstocks.

In recent times, especially within the past three decades, not only has oxygen analysis been required but there has also been a focus on the various types of oxygen functions in feedstocks.

Oxygen in organic compounds can occur in a variety of forms (Table 2.2), and it is not surprising that the more common oxygen-containing compounds occur in petroleum. The total oxygen content of crude oil is usually less than 2% by weight, although larger amounts have been reported, but when the oxygen content is phenomenally high it may be that the oil has suffered prolonged exposure to the atmosphere either during or after production. However, the oxygen content of petroleum increases with the boiling point of the fractions examined; in fact, the nonvolatile residua may have oxygen contents up to 8% by weight. Although these high-molecular-weight compounds contain most of the oxygen in petroleum little is known concerning their structure, but those of lower molecular weight have been investigated with considerably more success and have been shown to contain carboxylic acids and phenols.

The presence of acid substances (determined by several test methods as an acid number: ASTM D-664, ASTM D-974, ASTM D-1386, ASTM D-3242) in petroleum first appears to have been reported in 1874, and it was established

9 years later that these substances contained carboxyl groups and were carboxylic acids. These were termed naphthenic acids. Although alicyclic (naphthenic) acids appear to be the more prevalent, it is now well known that aliphatic acids are also present. In addition to the carboxylic acids, alkaline extracts from petroleum contain phenols.

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

In addition to the carboxylic acids and phenolic compounds, the presence of ketones, esters, ethers, and anhydrides has been claimed for a variety of crude oils. However, the precise identification of these compounds is difficult because most of them occur in the higher-molecular-weight nonvolatile residua. They are claimed to be products of the air blowing of the residua, and their existence in virgin petroleum may yet need to be substantiated.

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

2.3.2.3. *Nitrogen Compounds*

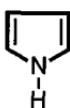
As with sulfur and oxygen, there are several tests to determine the amount of nitrogen in crude oil and its products but the identification of the various nitrogen functions is more difficult.

However, nitrogen in petroleum is classified as basic and nonbasic. The basic nitrogen compounds (Table 2.3), which are composed mainly of pyridine homologues and occur throughout the boiling ranges, have a decided tendency to exist in the higher-boiling fractions and residua. The nonbasic nitrogen compounds, which are usually of the pyrrole, indole, and carbazole types, also occur in the higher-boiling fractions and residua.

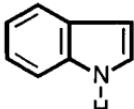
In general, the nitrogen content of crude oil is low and generally falls within the range 0.1–0.9%, although early work indicates that some crude oils may contain up to 2% nitrogen. However, crude oils with no detectable nitrogen or even trace amounts are not uncommon, but in general the more asphaltic the oil, the higher its nitrogen content.

Table 2.3. Types and Nomenclature of Organic Nitrogen Compounds*Nonbasic*

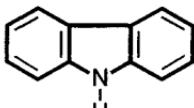
Pyrrole

 C_4H_5N 

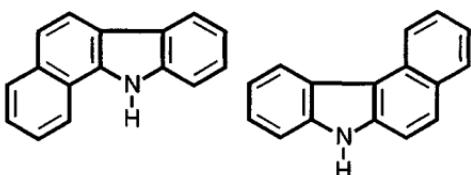
Indole

 C_8H_7N 

Carbazole

 $C_{12}H_9N$ 

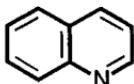
Benzo(a)carbazole

 $C_{16}H_{11}N$ *Basic*

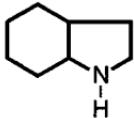
Pyridine

 C_5H_5N 

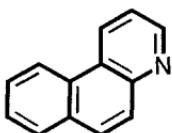
Quinoline

 C_9H_7N 

Indoline

 C_8H_9N 

Benzo(f)quinoline

 $C_{13}H_9N$ 

Insofar as a correlation exists between the sulfur content and API gravity of crude oils, there also exists a correlation between nitrogen content and the API gravity of crude oils (Speight, 1999, 2000). It also follows that there is an approximate correlation between the nitrogen content and the carbon residue: the higher the carbon residue, the higher the nitrogen content. The presence of nitrogen in petroleum is of much greater significance in refinery operations than might be

expected from the small amounts present. Nitrogen compounds can be responsible for the poisoning of cracking catalysts, and they also contribute to gum formation in such products as domestic fuel oil. The trend in recent years toward cutting deeper into the crude to obtain stocks for catalytic cracking has accentuated the harmful effects of the nitrogen compounds, which are concentrated largely in the higher-boiling portions (Gray, 1994; Speight, 2000).

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

2.3.2.4. *Porphyrins*

Porphyrins are a naturally occurring chemical species that have been known to exist in petroleum for more than 60 years (Falk, 1964; Smith, 1975; Branthaver, 1990). They are given separate consideration in this section because of their uniqueness as separate and distinct chemical entities. They are not usually considered among the usual nitrogen-containing constituents of petroleum, nor are they considered a metallo-containing organic material that also occurs in some crude oils. As a result of these early investigations, there arose the concept of porphyrins as biomarkers that could establish a link between compounds found in the geosphere and their corresponding biological precursors (Treibs, 1934; Glebovskaya and Volkenshtein, 1948).

Porphyrins usually occur in the nonbasic portion of the nitrogen-containing concentrate. The simplest porphyrin is porphine, and it consists of four pyrrole molecules joined by methine ($-\text{CH}=$) bridges (Branthaver, 1990; Reynolds, 1998; Speight, 1999). The methine bridges establish conjugated linkages between the component pyrrole nuclei, forming a more extended resonance system. Although the resulting structure retains much of the inherent character of the pyrrole components, the larger conjugated system gives increased aromatic character to the porphine molecule (Falk, 1964; Smith, 1975).

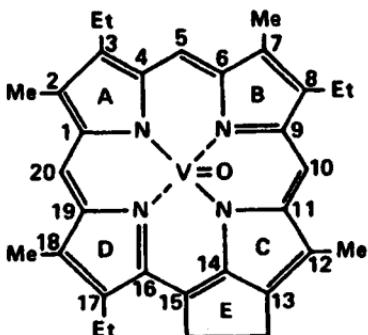


Figure 2.2. The formalized numbering system for porphyrins.

A large number of porphyrin compounds exist in nature or have been synthesized. Most of these compounds have substituents other than hydrogen on many of the ring carbons. The nature of the substituents on porphyrin rings determines the classification of a specific porphyrin compound into one of various types according to one common system of nomenclature (Fig. 2.2) (Bonnet, 1978; Branthaver, 1990; Reynolds, 1998). Porphyrins also have well-known trivial names or acronyms that are often in more common usage than the formal system of nomenclature.

When one or two double bonds of a porphyrin are hydrogenated, a chlorin or a phlorin is the result (Branthaver, 1990). Chlorins are components of chlorophylls, and they possess an isocyclic ring formed by two methylene groups bridging a pyrrolic carbon to a methine carbon. Geological porphyrins that contain this structural feature are assumed to be derived from chlorophylls. Etioporphyrins are also commonly found in geological materials and have no substituents (other than hydrogen) on the methine carbons. Benzoporphyrins and tetrahydrobenzoporphyrins have also been identified in geological materials. These compounds have either a benzene ring or a hydrogenated benzene ring fused onto a pyrrole unit.

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

Of all the metals in the periodic table, only vanadium and nickel have been proven definitely to exist as chelates in significant amounts in a large number of

crude oils and tar sand bitumen. The existence of iron porphyrins in some crude oils has been claimed (Franceskin et al., 1986). Geochemical reasons for the absence of substantial quantities of porphyrins chelated with metals other than nickel and vanadium in most crude oils and tar sand bitumen have been advanced (Hodgson et al., 1967; Baker, 1969; Baker and Palmer, 1978; Baker and Louda, 1986; Filby and Van Berkel, 1987; Quirke, 1987).

If the vanadium and nickel contents of crude oils are measured and compared with porphyrin concentrations, it is usually found that not all the metal content can be accounted for as porphyrins (Dunning et al., 1960; Reynolds, 1998). In some crude oils, as little as 10% by weight of total metals appears to be chelated with porphyrins. Only rarely can all measured nickel and vanadium in a crude oil be accounted for as porphyrinic (Erdman and Harju, 1963). Currently some investigators believe that part of the vanadium and nickel in crude oils is chelated with ligands that are not porphyrins. These metal chelates are referred to as nonporphyrin metal chelates or complexes (Crouch et al., 1983; Fish et al., 1984; Reynolds et al., 1987).

On the other hand, the amount of nonporphyrin metal in crude oils has been questioned (Goulon et al., 1984). There is the possibility that in such systems as the heavy crude oils, in which intermolecular associations are important, measurements of the porphyrin concentrations are unreliable and there is a tendency to undercount the actual values. However, for the purposes of this chapter it is assumed that nonporphyrin chelates exist in fossil fuels but the relative amount is as yet unknown.

Finally, during the fractionation of petroleum (Chapter 9), the metallic constituents (metalloporphyrins and nonporphyrin metal chelates) are concentrated in the asphaltene fraction. The deasphaltened oils (petrolenes and maltenes) (Chapter 9) contain smaller concentrations of porphyrins than the parent materials and usually very small concentrations of nonporphyrin metals.

2.3.2.5. Metallic Constituents

Metallic constituents are found in every crude oil, and the concentrations must be reduced to convert the oil to transportation fuel. Metals affect many upgrading processes and cause particular problems because they poison catalysts used for sulfur and nitrogen removal as well as other processes such as catalytic cracking (Wojciechowski and Corma, 1986; Peterson and Bell, 1987; Gray, 1994; Speight, 2000).

Thus the occurrence of metallic constituents in crude oil is of considerably greater interest to the petroleum industry than might be expected from the very small amounts present. Even minute amounts of iron, copper, and particularly nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yields of gasoline

(Wojciechowski and Corma, 1986; Peterson and Bell, 1987; Gray, 1994; Speight, 1999, 2000). In high-temperature power generators, such as oil-fired gas turbines, the presence of metallic constituents, particularly vanadium, in the fuel may lead to ash deposits on the turbine rotors, thus reducing clearances and disturbing their balance. More particularly, damage by corrosion may be very severe. The ash resulting from the combustion of fuels containing sodium and especially vanadium reacts with refractory furnace linings to lower their fusion points and so cause their deterioration.

Thus, the ash residue left after burning crude oil is caused by the presence of these metallic constituents, part of which occur as inorganic water-soluble salts (mainly chlorides and sulfates of sodium, potassium, magnesium, and calcium) in the water phase of crude oil emulsions. These are removed in the desalting operations, either by evaporation of the water and subsequent water washing or by breaking the emulsion, thereby causing the original mineral content of the crude to be substantially reduced. Other metals are present in the form of oil-soluble organometallic compounds as complexes, metallic soaps, or in the form of colloidal suspensions, and the total ash from desalinated crude oils is of the order of 0.1–100 mg/liter. Metals are generally found only in the nonvolatile portion of crude oil (Altgelt and Boduszynski, 1992; Reynolds, 1998).

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

Distillation concentrates the metallic constituents in the residua (Reynolds, 1998), although some can appear in the higher-boiling distillates, but the latter may be caused in part by entrainment. Nevertheless, there is evidence that a portion of the metallic constituents may occur in the distillates by volatilization of the organometallic compounds present in the petroleum. In fact, as the percentage of overhead obtained by vacuum distillation of a reduced crude is increased, the amount of metallic constituents in the overhead oil is also increased. The majority of the vanadium, nickel, iron, and copper in residual stocks may be precipitated

along with the asphaltenes by hydrocarbon solvents. Thus removal of the asphaltenes with *n*-pentane reduces the vanadium content of the oil by up to 95%, with substantial reductions in the amounts of iron and nickel.

2.3.2.6. *Nondistillable Constituents*

Although there have been attempts to identify the material boiling up to 705°C (1300°F) (Altgelt and Boduszynski, 1994), the nature of the chemical constituents in this boiling range remain largely unknown. Thus, on a boiling range basis, the most important range to the analytical chemist has been, for several decades, the nondistillable material (boiling point >565°C, >1050°F) that includes the nondistillable gas oil, the resins, and the asphaltenes.

The nondistillable residua consist of molecules of such low volatility that are the most complex of all crude oil fractions, consisting almost exclusively of heterocompounds, most of which contain several heteroatoms per molecule. They typically account for 30–60% of the total sulfur, 70–90% of the total nitrogen, and 80–90% of the total vanadium and nickel present in a crude oil. Saturates and aromatics together make up only a few weight percent of the nondistillable residua. Depending on the source and nature of the crude oil, approximately 40–70% by weight of the nondistillable residuum can be separated as an asphaltene fraction (Chapter 9).

The nondistillable residue can be separated into several fractions of increasing molecular weight and, thus, of increasing boiling point (Chapter 5). The nonasphaltene (soluble fraction) of a nondistillable residue is so complex that further separation by chromatography is highly inefficient.

The asphaltene constituents, being insoluble in low-boiling hydrocarbon liquids such as *n*-heptane, are also nondistillable, no matter from what source they are isolated. Because practically all analytical work on nondistillable compounds was done on asphaltenes, it is pertinent to use such work as a reference.

What little information we have on the composition of insolubles comes from elemental analysis, from spectroscopic methods such as infrared spectroscopy, nuclear magnetic resonance, and XANES spectroscopy, and from degradation followed by analysis of the fragments. The spectroscopic methods allow the determination of some functional groups and certain aspects of the hydrocarbon skeleton in the sample. The degradative approach leads to more detailed information on the fragments but not necessarily to quantitative data on the entire molecules (Chapter 7).

In the 1960s, a *chicken wire* model with large aromatic and naphthenic pericondensed ring systems was popular for asphaltenes. Modifications of this model still show up in review articles and other papers, although, generally, this view is no longer accepted (Sipeight, 1994b, 1999). These insoluble molecules are now seen as consisting of one or several relatively small ring clusters made up of only

a few condensed aromatic and naphthenic rings and containing polar heteroatom groups. In the larger molecules, several ring clusters, and maybe even single rings, are interconnected by paraffinic groups or chains and by sulfur linkages.

To a large extent, the nondistillable resin and asphaltene constituents have the same functionalities as simpler petroleum constituents comprising only one or two heteroatoms, except that they have them in higher concentration (Speight, 1994b, 1999). On the other hand, the high hydrogen deficiencies found in most high-boiling petroleum fractions seem to be incompatible with very small (1 or 2 ring) aromatic moieties. It is the presence of the heteroatoms (nitrogen and sulfur, with oxygen playing a lesser role) that contribute to the formation of high yields of coke from the asphaltene fraction. (Speight, 1994b, 1999).

On the basis of thermodynamic principles, the differences between asphaltenes and resins (soluble polar fraction) should be gradual rather than abrupt. This is indeed true (Speight, 1999 and references cited therein), and there are definite similarities between the constituents of the two fractions when the properties of asphaltenes and resins obtained from the same residue under identical conditions by means of three separation methods, namely, adsorption chromatography, are compared. This, together with the great dependence of asphaltene yields on alkane type and precipitation conditions, emphasizes the gradual nature of the shift in the composition of resins and asphaltenes.

The molecular weights of the hydrocarbon-soluble fraction of nondistillable residua can generally be determined by vapor pressure osmometry without any difficulty. However, the true molecular weight ranges of the insolubles are hard to determine. Most have molecular weight distributions ranging from about 500 to a few thousand daltons (Chapter 12). A strong tendency to aggregate makes vapor pressure osmometry using nonpolar solvents questionable. With polar solvents (such as pyridine and nitrobenzene), considerably lower molecular weight values are produced, and at elevated temperatures, the molecular weights are even lower.

Thus the true molecular weights of asphaltene constituents, free from aggregation and other interferences, are not accurately known, although estimations can be made using graphical methods (Speight, 1999).

The salient features of asphaltene science must be recalled and summarized at this point.

1. Asphaltenes differ in yield and composition depending not only on crude oil origin but also on type of residuum from which they have been precipitated (atmospheric or vacuum), the precipitant (*n*-pentane, *n*-heptane), and precipitation conditions (sample-to-precipitant ratio, addition of solvents such as benzene, temperature, agitation, and digestion time).
2. Asphaltenes are not a unique chemical compound group or compound class. They are a strictly operationally defined solubility fraction. The common phrases

asphaltene molecules or *asphaltene-type structures* are imprecise and can be misleading. The fraction consists of a large variety of constituents of unknown structure and wide range of molecular weight.

3. It is also possible to separate the asphaltene fraction (including the resins), into acids, bases, and neutral species. There are workers who advocate leaving the asphaltenes in the feedstock and performing such a chemical-type separation on the whole feedstock.

It is not the purpose of this book to enter the long debate about the pros and cons of determining an asphaltenes fraction in a feedstock. Item 3 above notwithstanding, the asphaltene must be recognized as the fraction that contains a high concentration of heteroatoms and especially metals and that has the most adverse effect on crude oil refining.

Knowing the amount of asphaltene fraction in a feedstock can, indeed, greatly help in assessing crude oil processability (Speight, 2000). The separation of this fraction using low-boiling hydrocarbons is a convenient shortcut for concentrating the most refractory petroleum constituents and determining their amount. It is also a very common procedure with many variations.

Throughout this book, the asphaltenes are considered as a separate fraction and are referred to as such. Certain analytical techniques can suffer when the asphaltenes are not first removed from the feedstock before application of the technique.

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CHAPTER

3

CLASSIFICATION

3.1. INTRODUCTION

Petroleum (also called *crude oil*) is a mixture of gaseous, liquid, and solid hydrocarbon compounds that occurs in sedimentary rock deposits throughout the world and also contains small quantities of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metallic constituents (Bestougeff, 1967; Colombo, 1967; Hobson and Pohl, 1973; Thornton, 1977; Considine and Considine, 1984; Speight, 1999). Thus it might be anticipated that the classification of petroleum as a hydrocarbon mixture should follow from this definition. However, because of the apparent (contradictory) *similarity* and *diversity* of crude oil this is not the case, and some clarification is required.

Officially, petroleum is defined (Chapter 1) as 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, 1998). In more specific terms, petroleum has also been defined (ITAA, 1936) as:

- any naturally occurring hydrocarbon, whether in a liquid, gaseous, or solid state;
- any naturally occurring mixture of hydrocarbons, whether in a liquid, gaseous, or solid state; or
- any naturally occurring mixture of one or more hydrocarbons, whether in a liquid, gaseous, or solid state, and one or more of the following: hydrogen sulfide, helium, and carbon dioxide.

The definition includes any petroleum as defined by paragraph (1), (2) or (3) that has been returned to a natural reservoir.

These definitions of petroleum are clear in their meaning, but attempting to classify petroleum takes on other dimensions. As noted, these are the dimensions of similarity and diversity. Thus the analytical chemist, although provided with a host of analytical techniques and tools, will find himself/herself stymied when attempting to classify petroleum on the basis of a single or simple property. Attempts have been made to classify petroleum using a single property such as API gravity (ASTM D-287, ASTM D-1298, ASTM D-3142) or the kinematic viscosity (ASTM D-445) with only very limited success. The precision and accuracy

of the analytical methods calls into question the real meaning of any such data (Chapters 4 and 5).

On the other hand, the classification of coal involves a series of steps with well-defined procedure and guidelines at the end of which a classification is achieved (ASTM D-388). In fact, there are several classification systems for coal (Speight, 1994) that have evolved in various countries and that can be applied successfully and compared knowledgeably with each other—not so for petroleum; please read on!

One of the major disadvantages in attempting a *classification of petroleum*, vis-à-vis the classification of coal, is that the elemental (ultimate) composition of petroleum (Chapter 2) is not reported to the same extent as it is for coal (Lowry, 1945, 1963; Meyers, 1981; Hessley, 1990; Speight, 1994) and does not have the same spread of elemental content. The proportions of the elements in petroleum vary only slightly over fairly narrow limits despite the wide variation in physical properties from the lighter, more mobile (conventional) crude oil to bitumen at the other extreme. Thus, as a result of the wide variety of organic constituents and physical conditions that can play a role in the formation of petroleum, it is surprising that there is not a wider variation in the composition of petroleum.

Indeed, there are many general definitions that are really descriptions of petroleum, heavy oil, and bitumen (Chapter 1), but none are sufficiently accurate to convey an accurate meaning or to be considered as part of a classification system. Furthermore, there are several classification methods that are used for chemical characterization according to functional groups distribution (ASTM F-1186), infrared absorption spectroscopy (ASTM E-204), the viscosity of industrial lubricants (ASTM D-2422), petroleum waxes for use in rubber compounding (ASTM D-4924), and the ultraviolet absorptivity of petroleum products (ASTM D-2000). However, none of these methods is adequate to the task of classifying petroleum. For the most part, correctly or incorrectly, the classification of petroleum has been forced into reliance on physical properties. In some cases, one physical property has been used. In other cases, a combination of physical properties has been used.

Petroleum does exhibit a wide range of physical properties (Chapters 4, 5, and 6), but, unlike coal, the use of these properties in attempts at classification is less well defined than the use of the properties in the various coal classification systems (ASTM D-388; Speight, 1994). However, there are correlations that can be made between various physical properties presenting relationships for various crude oils, and even though properties such as viscosity, density, boiling point, and color of petroleum may vary, the ultimate or elemental analysis varies, as already noted, over a narrow range for a large number of petroleum samples (Chapter 2). Therefore, it becomes a matter of what to correlate with what for a functional classification system.

In fact, a functional classification of petroleum into conventional petroleum, heavy oil, and tar sand bitumen involves not only an inspection of several properties but also an additional and workable parameter, reference to the method of recovery (page 78). Acknowledgment of the recovery method not only adds a new dimension to the data derived by analytical testing but also identifies and qualifies the nature of the material under investigation.

Thus it is the purpose of this chapter to review the classification methods that have evolved over time and to present them for further consideration as the culmination and conjunction of two or more analytical methods. All of these methods involve determination of the relevant properties of petroleum through analytical techniques, many of which are covered in the various chapters throughout this book. No attempt is made in this chapter to reference all of the methods; the more pertinent methods are noted below.

3.2. CLASSIFICATION SYSTEMS

The original methods of classification arose because of commercial interest in petroleum type and were a means of providing refinery operators with a rough guide to processing conditions. It is therefore not surprising that systems based on a superficial inspection of a physical property, such as specific gravity or API (Baumé) gravity (ASTM D-287, ASTM D-1298, ASTM D-3142) (Chapter 4), are easily applied and are actually used to a large extent in expressing the quality of crude oils. Although such a system is *approximately* indicative of the general character of a crude oil, as long as materials of one general type are under consideration, application as a general classification method is more difficult and often fraught with errors. However, generally speaking, among crude oils from a particular area, an oil of 40° API gravity (specific gravity = 0.825) is usually more valuable than one of 20° API gravity (specific gravity = 0.934) because it contains a higher proportion of lower-boiling fractions (e.g., naphtha) and lesser amounts of the higher-boiling (undesirable) asphaltic constituents.

However, in terms of petroleum classification using the elemental composition, the carbon content is relatively constant, whereas the hydrogen and heteroatom contents are responsible for the major differences between petroleum classes. The nitrogen, oxygen, and sulfur can be present in only trace amounts in some petroleum, which as a result consists primarily of hydrocarbons. On the other hand, a crude oil containing 9.5% heteroatoms may contain essentially no true hydrocarbon constituents because the constituents contain *at least one or more* nitrogen, oxygen, and/or sulfur atom within the molecular structures.

A case might be made for using the elemental composition as a means of classification. Indeed, the method might be workable when comparing specific families of crude oil from a particular region, but the end result offers very little

meaning when applied to petroleum in general. One has to question whether a hydrogen-to-carbon atomic ratio of 1.60 for one crude oil is really that much different from a hydrogen-to-carbon ratio of 1.65 of another crude oil when the heteroelements vary but the API gravity, for example, might be the same for both crude oils. And the classification web can become even more tangled.

There has been more success in using the molecular types in crude oil as a means of classification (page 70). The molecular species in petroleum vary from simple hydrocarbon species (in the majority) to very complex organic molecules containing atoms of carbon, hydrogen, nitrogen, oxygen, and sulfur (in the minority) as well as trace amounts of metals such as vanadium, nickel, iron, and copper (Chapter 2). However, classification using the various metals must be approached with caution because many crude oils pick up errant (nonindigenous) metal species during pipelining and storage. One would not wish to classify petroleum on the basis of pipeline construction or storage tank components!

The molecular complexity of petroleum is further illustrated by the number of potential isomers, i.e., molecules having the same atomic formula, that can exist for a given number of paraffinic carbon atoms, which increases rapidly as molecular weight increases:

Carbon atoms per hydrocarbon	Number of isomers
4	2
8	28
12	355
18	60,523

This same increase in number of isomers with molecular weight also applies to the other molecular types present. Because the molecular weights of the molecules found in petroleum can vary from that of methane (CH_4 ; molecular weight 16) to several thousand (Speight et al., 1985), it is clear that the heavier nonvolatile fractions can contain virtually unlimited numbers of molecules. However, in reality, the number of molecules in any specified fraction is limited by the nature of the precursors of petroleum, their chemical structures, and the physical conditions that are prevalent during the maturation (conversion of the precursors) processes.

Attempting to use specific compound types as a means of classification has met with some success but requires careful and detailed analysis. Gas chromatography can play a major role in such a system but may be better limited to boiling range analysis (ASTM D-2887) and to specific fractions (ASTM D-3710, ASTM D-5134) and response factors (ASTM D-4626). When feedstocks such as heavy oil and bitumen are considered, gas chromatography does have a role, but it is somewhat limited by the nature of the feedstock. Thus one might be able to classify

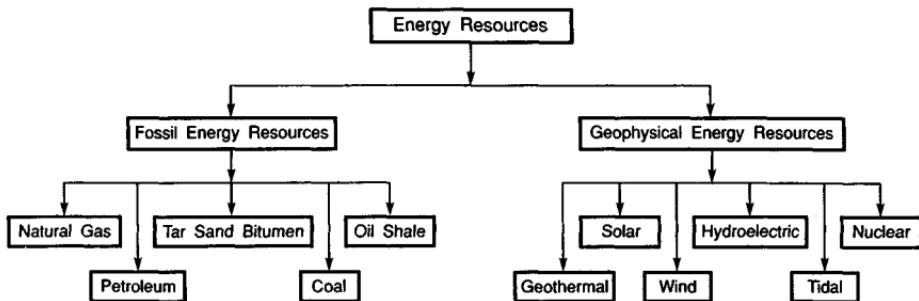


Figure 3.1. Classification of energy resources.

lower-boiling fractions on the basis of the hydrocarbon content of certain fractions (see also Chapter 3), but the system would fall short when applied to heavy oil and bitumen.

3.2.1. Classification as a Hydrocarbon Resource

Petroleum is referred to generically as a *fossil energy resource* (Fig. 3.1) and is further classified as a *hydrocarbon resource*.

Resources can be subdivided and classified as *discovered resources* or *undiscovered resources* (Speight, 1999), although how anyone can put meaningful figures to a term such as *undiscovered resources* is beyond the scope of this book and the mental capacity of many scientists and engineers, the author included!

Of the *discovered resources*, classification is further achieved by consideration of whether or not a discovered resource contains *nonrecoverable material* or *recoverable material*. Of the recoverable material, further subdivision into various subclasses of reserves applies where the attachment of adjectives such as *proven* (e.g., *proven reserves*) and *probable* (e.g., *probable reserves*) also applies. Again, the derivation of meaningful numbers for terms such as *probable reserves* is beyond the scope of this book and the mental capacity of many scientists and engineers, the author included! Be that as it may, for the purposes of this text the adjective of consequence is *proven* (*proved*), and we will not dabble in numbers for resource or reserve estimates that border on popular *fiction*.

To continue, for illustrative (or comparative) purposes in this text, coal and oil shale kerogen have also been included in this classification. However, the inclusion of coal and oil shale under the broad classification of *hydrocarbon resources* has required (incorrectly) that the term *hydrocarbon* be expanded to include the macromolecular nonhydrocarbon heteroatomic species that constitute coal and oil shale kerogen. Use of the term *organic sediments* would be more correct (Fig. 3.2). The inclusion of coal and oil shale kerogen in the category of hydrocarbon resources is due to the fact that these two natural resources (coal and oil shale

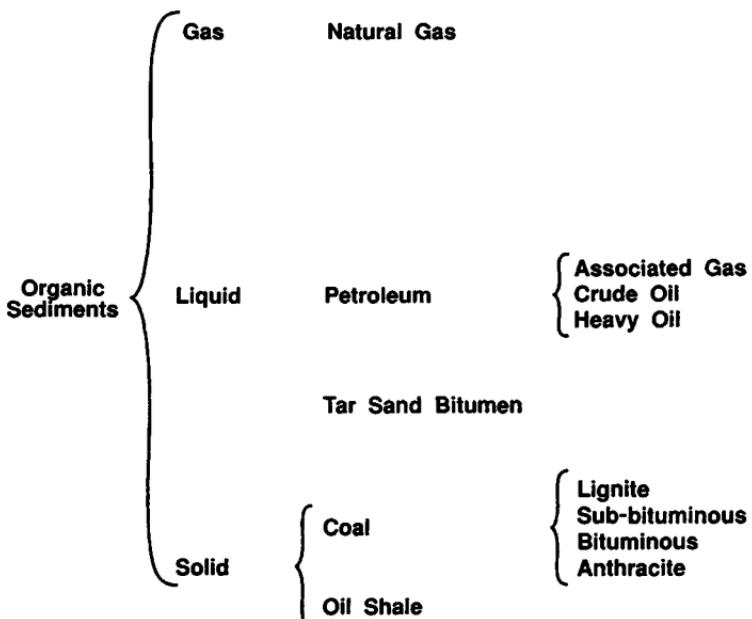


Figure 3.2. Classification of organic sediments (from Speight, 1999).

kerogen) will produce hydrocarbons on high-temperature processing. Therefore, if coal and oil shale kerogen are to be included in the term hydrocarbon resources, it is more appropriate that they be classed as *hydrocarbon-producing resources* under the general classification of *organic sediments* (Fig. 3.3).

Thus, fossil energy resources divide into two classes:

1. naturally occurring hydrocarbons (petroleum, heavy oil, natural gas, and natural waxes); and
2. hydrocarbon sources (bitumen, oil shale, and coal) that may be made to generate hydrocarbons by the application of conversion processes.

Both classes may be aptly, and more correctly, described as organic sediments. Petroleum and heavy oil fall conveniently and correctly into the first category listed.

The determination that petroleum can be classed as a hydrocarbon resource is not beyond the scope of reality. Indeed, petroleum (and its relative *heavy oil*) contains high proportions of individual hydrocarbons (Nelson, 1958; Gruse and Stevens, 1960; Bestougeff, 1967; Hobson and Pohl, 1973; Speight, 1999; and references cited in all of these texts).

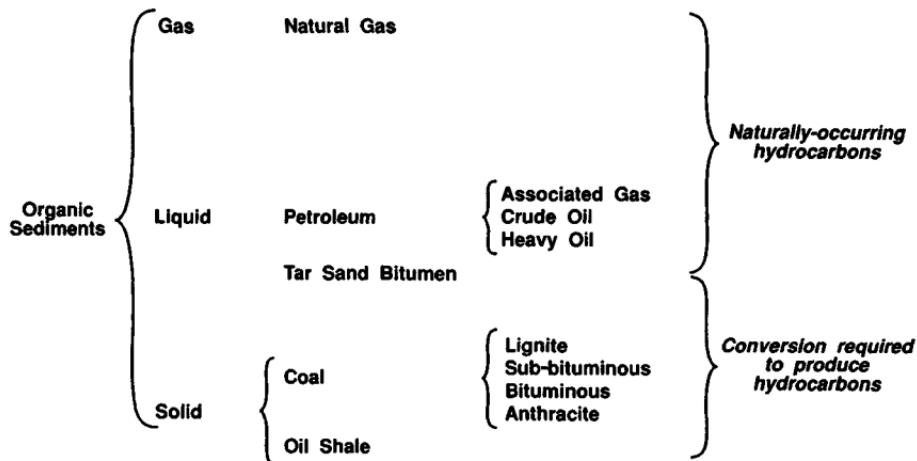


Figure 3.3. Classification of organic sediments based on hydrocarbon content and hydrocarbon potential (from Speight, 1999).

In summary, the classification of petroleum as a naturally occurring mixture of hydrocarbons is possible by virtue of the fact that it can be separated into original hydrocarbon constituents that have not been altered by any applied process. Naturally occurring hydrocarbons are major contributors to the composition of petroleum. Coal and kerogen do not enjoy this means of separation, and methods of thermal decomposition must be applied before hydrocarbons are produced. Tar sand bitumen is analogous to coal and oil shale kerogen insofar as methods of thermal decomposition must be applied to the bitumen to produce hydrocarbons. These hydrocarbons did not exist in the natural state in the reservoir and are derivatives of the thermal process. For commercial purposes, the hydrocarbons produced from bitumen by thermal processes are collectively called *synthetic crude oil* (Speight, 1990).

Thus, using the concept of whether a resource is a naturally occurring hydrocarbon source (natural gas, petroleum, heavy oil) or whether the resource requires application of heat (tar sand bitumen, coal, oil shale kerogen) to produce hydrocarbon products enables a start to be made in the classification system.

From this start it is possible to move to the next system of classification that involves an examination of the crude oil on the basis of chemical composition.

3.2.2. Classification by Chemical Composition

Composition refers to the specific mixture of chemical compounds that constitute petroleum. The composition of these materials is related to the nature and mix of the

organic material that generated the hydrocarbons. Composition is also subject to the influence of natural processes such as migration (movement of oil from source rock to reservoir rock), biodegradation (alteration by the action of microbes), and water washing (effect of contact with water flowing in the subsurface) on that composition. Thus petroleum is the result of the metamorphosis of natural products as a result of chemical and physical changes imparted by the prevailing conditions at a particular locale (Speight, 1999).

Petroleum varies in appearance from a thin (mobile), nearly colorless liquid to a thick (viscous), almost black oil. The specific gravity (at 15.6°C, 60°F) varies correspondingly from about 0.75 to 1.00 (57–10° API), with the specific gravity of most crude oils falling in the range from 0.80 to 0.95 (45–17° API). Thus it is not surprising that petroleum varies in composition from one oil field to another, from one well to another in the same field, and even from one level to another in the same well. This variation can be both in molecular weight and in the types of molecules present in petroleum. Thus petroleum may well be described as a mixture of organic molecules drawn from a wide distribution of molecular types that lie within a wide distribution of molecular weights.

By definition, *a hydrocarbon contains carbon and hydrogen only* (Roberts and Caserio, 1964; Morrison and Boyd, 1973; Fessenden and Fessenden, 1990), with the inclusion of any other elements (e.g., nitrogen, oxygen, and sulfur) causing differences in properties and the inclusion of functional groups into the original hydrocarbon system (ASTM F-1186).

Thus, on the other hand, if an organic compound contains nitrogen, and/or sulfur, and/or oxygen, and/or metals, it is a heteroatomic compound and not a hydrocarbon. Organic compounds containing heteroelements (elements such as nitrogen, oxygen, and sulfur) in addition to carbon and hydrogen are defined in terms of the locations of these heteroelements within the molecule. In fact, to a large extent, the heteroatomic function determines the chemical and physical reactivity of the heteroatomic compounds (Roberts and Cesario, 1964; Morrison and Boyd, 1973; Fessenden and Fessenden, 1990), and the chemical and physical reactivity of the heteroatomic compounds is quite different from the chemical and physical reactivity of the hydrocarbons.

Naturally occurring hydrocarbons are those molecules that contain carbon and hydrogen only and that occur in nature. The term *naturally occurring hydrocarbons* does not apply to those hydrocarbons that are produced by applied processes such as the thermal decomposition of coal to produce liquids and gases or the retorting (thermal decomposition) of oil shale kerogen to produce shale oil.

Petroleum is a *naturally occurring hydrocarbon* insofar as it contains compounds that are composed of carbon and hydrogen only (Hobson and Pohl, 1973; Considine and Considine, 1984) and do not contain any heteroatoms (nitrogen, oxygen, and sulfur as well as compounds containing metallic constituents, particularly

vanadium, nickel, iron, and copper). The hydrocarbons found in petroleum are classified into the following types:

1. *paraffins*: saturated hydrocarbons with straight or branched chains but without any ring structure;
2. *cycloparaffins (naphthenes)*: saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as *alicyclic hydrocarbons*);
3. *aromatics*: hydrocarbons containing one or more aromatic nuclei such as benzene, naphthalene, or phenanthrene ring systems that may be linked up with (substituted) naphthalene rings and/or paraffinic side chains.

On this basis, petroleum may have some value in the crude state, but when refined it provides fuel gas, petrochemical gas (methane, ethane, propane, and butane), transportation fuel (gasoline, diesel fuel, and aviation fuel) solvents, lubricants, asphalt, and many other products.

In addition to the hydrocarbon constituents, petroleum does contain heteroatomic (nonhydrocarbon) species, but they are in the minority compared to the macromolecular heteroatom-containing kerogen (Costantinides and Arich, 1967; Tissot and Welte, 1978).

A widely used classification of petroleum distinguishes between crude oils either on a *paraffin base* (paraffin constituents) or on an *asphalt base* (cycloparaffin or naphthene constituents) (Fig. 3.4) and arose because paraffin wax separates from some crude oils on cooling but other oils show no separation of paraffin wax on cooling. The terms *paraffin base* and *asphalt base* were introduced and have remained in use (van Nes and van Westen, 1951; Nelson, 1958; Hobson and Pohl, 1973). To accommodate crude oils that were neither *paraffin base* nor *naphthene base*, the term *intermediate base* is applied.

The presence of paraffin wax is usually reflected in the paraffinic nature of the constituent fractions, and a high asphaltic content corresponds with the so-called naphthenic properties of the fractions. As a result, the misconception that paraffin-base crude oils consist mainly of paraffins and asphalt-base crude oils mainly of cyclic (or naphthenic) hydrocarbons has arisen. In addition to paraffin- and asphalt-base oils, a mixed base class had to be introduced to describe those oils that leave a mixture of bitumen and paraffin wax as a residue by nondestructive distillation.

In practice, a distinction is often made between light and heavy crude oils (indicating the proportion of low-boiling material present), which, in combination with the preceding distinction (paraffinic, asphaltic, and so on), doubles the number of possible classes.

The United States Bureau of Mines (USBM, 1950) designated eight bases of crude oil according to the character of a key fraction boiling at 275–300°C

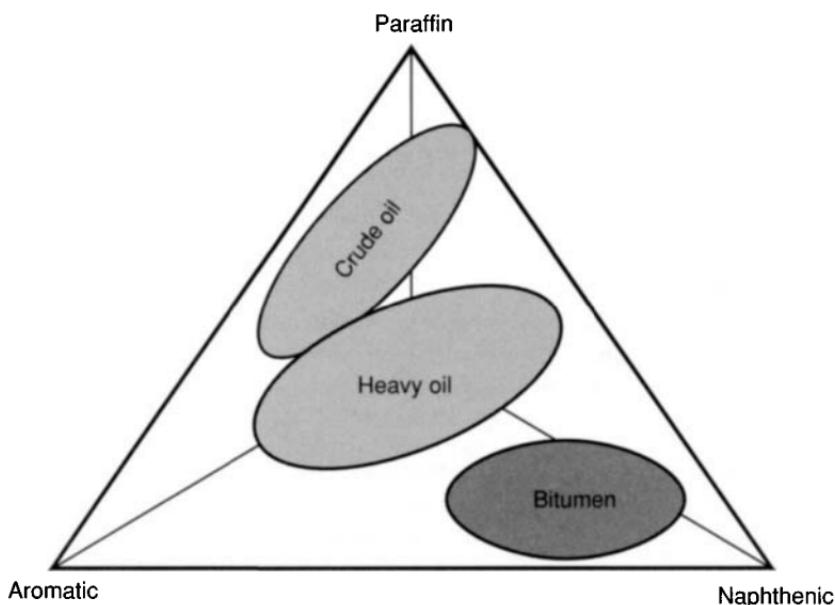


Figure 3.4. Classification based on hydrocarbon type.

(527–572°F) at 40 mm pressure (equivalent to approximately 390–415°C, 733–779°F at 7060 mm pressure).

For a time, this system of classification proved adequate to the task, and it may even still be used in some laboratories. The advent of different types of crude oil (heavy oil) and bitumen as refinery feedstocks has changed the emphasis on this system. In-house classification of crude oil has depended on the various refinery scenarios and the need for the various end products.

3.2.3. Correlation Index

An early attempt to give the classification system a quantitative basis suggested that a crude should be called *naphthenic (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 3.1).

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

Table 3.1. 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

chemical information is often desirable and can be supplied by means of the *correlation index (CI)*.

The correlation index, developed by the US Bureau of Mines, is based on the plot of specific gravity versus the reciprocal of the boiling point in degrees Kelvin ($K = {}^{\circ}\text{C} + 273$). For pure hydrocarbons, the line described by the constants of the individual members of the normal paraffin series is given a value of $\text{CI} = 0$ and a parallel line passing through the point for the values of benzene is given as $\text{CI} = 100$ (Fig. 3.5); thus,

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

where K for a petroleum fraction is the average boiling point determined by the standard Bureau of Mines distillation method and d is the specific gravity (Gruse and Stevens, 1960).

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.

It is also possible to describe a crude oil by an expression of its chemical composition on the basis of the correlation index data for its middle portions (Fig. 3.6).

The position of a crude on this scale is determined by the average correlation index for its fractions boiling between 200°C (390°F) at atmospheric pressure and 275°C (525°F) at 40 mm, and the paraffinic, or cyclic, nature of the fractions, and thereby the nature of the bulk of the crude, are expressed directly. The height of the vertical bar above the horizontal indicates the wax content of the heavy gas oil and light lubricating fractions of that crude, and hence the crystalline wax content of the crude can be assessed. The length of each bar below the horizontal is a measure of the carbon residue (Conradson) of the nonvolatile residuum (ASTM D-189, ASTM D-2416) and therefore serves to indicate the asphalt content of each residuum and, thus, the content of each crude oil. By combining these chemical

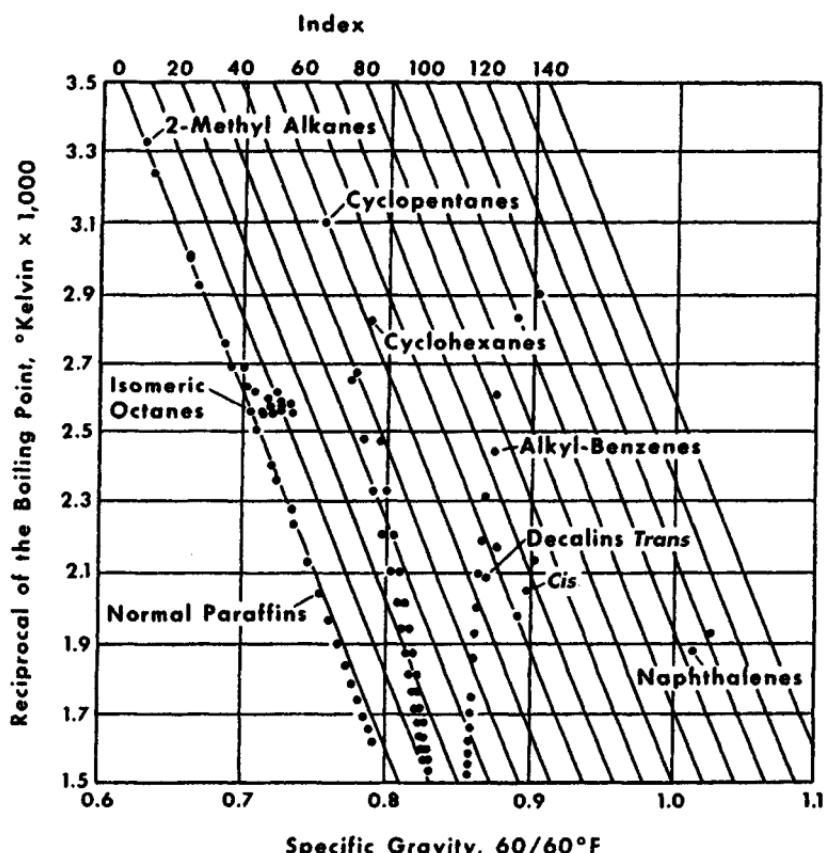


Figure 3.5. Reference data for the correlation index (from Speight, 1999).

indications with a qualitative expression of the results achieved by conventional refining, reasonable assessment can be obtained of a petroleum in relation to both composition and application.

3.2.4. Density

Density (specific gravity) (Chapter 4) has been, since the early years of the industry, the principal and often the only specification of crude oil products and was taken as an index of the proportion of gasoline and, particularly, kerosene present. As long as only one kind of petroleum was in use the relations were approximately true, but as crude oils with other properties were discovered and came into use, the significance of density measurements disappeared. Nevertheless, crude oils of particular types are still rated by gravity, as are gasoline and naphtha within certain limits of other properties.

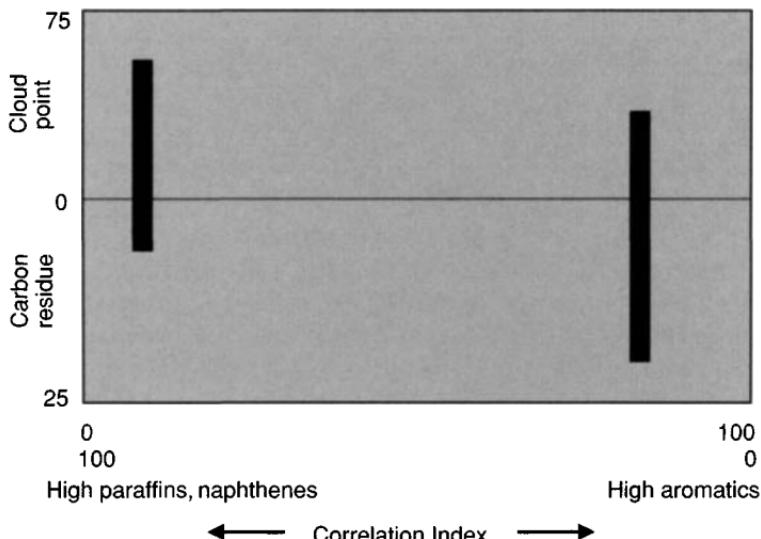


Figure 3.6. Correlation index and crude oil composition.

The use of density values has been advocated for quantitative application with a scheme based on the American Petroleum Institute (API) gravity of the 250–275°C (480–525°F, 760 mm) and the 275–300°C (525–570°F, 40 mm) distillation fractions (Table 3.2). Indeed, investigation of crude oils from worldwide sources showed that 85% fell into one of the three classes: *paraffin base*, *intermediate base*, or *naphthene base*.

Classification of heavy oils according to characterization gravity also has been proposed. This is defined as the arithmetic average of the instantaneous specific gravity of the distillates boiling at 177°C (350°F), 232°C (450°F), and 288°C (550°F) vapor line temperature at 25-mm pressure in a true boiling point distillation.

In addition, a method of petroleum classification based on other properties, as well as the density, of selective fractions has been developed. The method consists of a preliminary examination of the aromatic content of the fraction boiling up to 145°C (295°F), as well as that of the asphaltene content, followed by a more detailed examination of the chemical composition of the naphtha (bp <200°C, <390°F). For this examination, a graph is used that is a composite of curves expressing the relation between percentage distillate from the naphtha, the aniline point, refractive index, specific gravity, and the boiling point. The aniline point after acid extraction is included to estimate the paraffin-to-naphthene ratio.

Conventional crude oil and heavy oil have also been defined very generally in terms of physical properties. For example, the class of heavy oils was considered

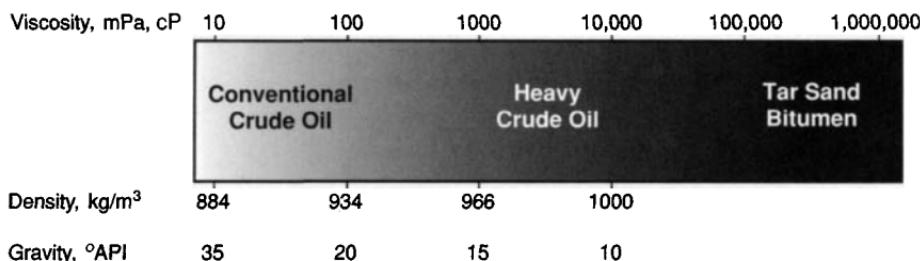
Table 3.2. Classification According to API Gravity (Adapted from Speight, 1999)

Fraction				
250–270°C 480–520°F		275–300°C 525–570°F		
API Gravity	Type	API Gravity	Type	Classification
>40.0	Paraffin	>30.0	Paraffin	Paraffin
>40.0	Paraffin	20.1–29.9	Intermediate	Paraffin-intermediate
33.1–39.9	Intermediate	>30.0	Paraffin	Intermediate-paraffin
33.1–39.9	Intermediate	20.1–29.9	Intermediate	Intermediate
33.1–39.9	Intermediate	<20.0	Naphthene	Intermediate-naphthene
<33.0	Naphthene	20.1–29.9	Intermediate	Naphthene-intermediate
<33.0	Naphthene	<20.0	Naphthene	Naphthene
>44.0	Paraffin	<20.0	Naphthene	Paraffin-naphthene
33.0	Naphthene	>30.0	Paraffin	Naphthene-paraffin

to be those petroleum-type materials that had gravity somewhat less than 20° API, with the heavy oils falling into the API gravity range of 10–15° (e.g., Cold Lake crude oil = 12° API) and bitumen falling into the 5–10° API range (e.g., Athabasca bitumen = 8° API). Residua vary depending on the temperature at which distillation is terminated. Atmospheric residua are usually in the 10–15° API range, and vacuum residua are in the range of 2–8° API (Speight, 2000).

There have been several recent noteworthy attempts to classify crude oil (Bestougeff et al., 1984; Danyluk et al., 1984; Gibson, 1984; Khayan, 1984) using one or more of the general physical properties of crude oils. One method uses divisions by API gravity, which is generally used by most workers, and also uses viscosity data (Khayan, 1984). This method is essentially a more formal attempt in which specific numbers are applied (Fig. 3.7).

Several attempts have been made to discriminate or classify heavy oil and bitumen on the basis of viscosity. For example, it has been recommended that

**Figure 3.7.** Viscosity-density relationship of crude oil, heavy oil, and bitumen (from Speight, 1999).

viscosity data be applied to differentiate between petroleum and tar sand bitumen (Khayan, 1984), thereby offering a means of classifying these two natural products. The viscosity cutoff point is suggested to be 10,000 centipoises (cp), below which the material is classified as petroleum and above which the material is classified as tar sand bitumen. This method is essentially a more formal attempt in which specific numbers are applied. In addition, the scale can be used for other feedstocks, such as the conventional petroleum and residua. However, as already noted (page 61), petroleum classification (or, for that matter, any classification system) that is based on a single measurement is at the mercy of the analyst and the errors that are inherent in the method.

The *line demarcation* of 10,000 cp is impractical because there is no one property of a hydrocarbon that can be used to define tar sand bitumen. In addition, the use of 10,000 cp as the line of demarcation is difficult to accept. Publication in conference proceedings and in books, where it is used for discussion purposes, is not a sign of accuracy or general acceptance. Rather, these publications show that the advisability of the 10,000 cp line has been a topic of question. Indeed, the accuracy (reproducibility or repeatability or precision) of the determination of viscosity almost refutes the use of such numbers. For example, at an accuracy of at least $\pm 5\%$ a value of 10,000 cp is, in reality a value between 9500 and 10,500 cp. For extremely viscous materials such as bitumen the margin of accuracy may be even higher than $\pm 5\%$, and therefore a greater range is represented. In fact, this indicates that a line of demarcation is of little value for these materials.

Indeed, in the author's experience, if viscosity were to be accepted as part of the definition, any such line of demarcation would have to be much higher (at least on the order of 50,000 cp or even 100,000 cp). However, this still does not move away from the use of a single physical property that is subject to errors that are inherent in the method of measurement.

3.2.5. Carbon Distribution

A method for the classification of crude oils can only be efficient, first, if it indicates the distribution of components according to volatility, and second, if it indicates one or more characteristic properties of the various distillate fractions. The distribution according to volatility has been considered the main property of petroleum, and any fractionating column with a sufficient number of theoretical plates may be used for recording a curve in which the boiling point of each fraction is plotted against the percentage by weight.

However, for the characterization of the various fractions of petroleum, the use of the *n-d-M* method [n = refractive index, d = density, M = molecular weight (Chapter 11)] is suggested. This method enables determination of the carbon distribution and thus indicates the percentage of carbon in aromatic structure (%C_A),

the percentage of carbon in naphthenic structure ($\%C_N$), and the percentage of carbon in paraffinic structure ($\%C_P$). The yields over the various boiling ranges can also be estimated; for example, in the lubricating oil fractions the percentage of carbon in paraffinic structure can be divided into two parts, giving the percentage of carbon in normal paraffins ($\%C_{nP}$) and the percentage of carbon in paraffinic side chains. The percentage of normal paraffins present in lubricating oil fractions can be calculated from the percentage of normal paraffinic carbon ($\%C_{nP}$) by multiplication by a factor that depends on the hydrogen content of the fractions.

It is also possible to extrapolate the carbon distribution to the gasoline range on the one hand and to the residue on the other hand. A high value of $\%C_A$ at 500°C (930°F) boiling point usually indicates a high content of asphaltenes in the residue, whereas a high value of $\%C_{nP}$ at 500°C (930°F) boiling point usually indicates a waxy residue.

3.2.6. Viscosity-Gravity Constant

This parameter, along with the Universal Oil Products characterization factor, has been used to some extent as a means of classifying crude oils. Both parameters are usually used to give an indication of the paraffinic character of the crude oil, and both have been used, if a subtle differentiation can be made, as a means of petroleum characterization rather than for petroleum classification.

Nevertheless, the viscosity-gravity constant was one of the early indices proposed to characterize (or classify) oil types:

$$vgc = 10d - 1.0752 \log(\nu - 38)/10 - \log(\nu - 38)$$

where d is the specific gravity 60°/60°F and ν is the Saybolt viscosity at 39°C (100°F). For heavy oil where the low-temperature viscosity is difficult to measure, an alternative formula,

$$vgc = d - 0.24 - 0.022 \log(\nu - 35.5)/0.755$$

has been proposed in which the 99°C (210°F) Saybolt viscosity is used. The two do not agree well for low-viscosity oils. However, the viscosity-gravity constant is of particular value in indicating a predominantly paraffinic or cyclic composition. The lower the index number, the more paraffinic is the stock; for example, naphthenic lubricating oil distillates have $vgc = 0.876$ and the raffinate obtained by solvent extraction of lubricating oil distillate has $vgc \approx 0.840$.

3.2.7. UOP Characterization Factor

This factor is perhaps one of the more widely used derived characterization or classification factors and is defined by the formula

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

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

Finally, all the classification systems mentioned here are based on the assumption that an oil can be more or less characterized by the properties of one or a few fractions. However, the properties of certain fractions of a crude oil are definitely not always reflected in those of other fractions of the same oil. Indeed, some crude oils have a different chemical character in low-boiling and high-boiling fractions, and any method of classification in which the properties of a certain fraction are extrapolated to the whole crude oil must be applied with caution because serious errors can arise.

In fact, it appears unlikely that it will ever be possible to have a single classification method that will accommodate all crude oils. It is usually necessary to combine a boiling range analysis with the carbon distribution in the various fractions to gain a reasonable perspective of the crude, which even then gives only an estimation of the division of products that might be expected in the refinery.

3.3. MISCELLANEOUS SYSTEMS

Predicting the behavior of crude oil during production and refining operations requires a detailed knowledge of the structure of crude oil (Chapter 14). The classical approach of correlating properties with structural types has proved to be of some value. However, determining the structural types that will dominate the properties of crude oil is often difficult. Thus other classification systems have evolved.

For example, crude oil can be assessed or defined by its relative *distillation characteristics* (Table 3.3), but the properties and character of a residuum from any particular petroleum depend on the temperature at which the distillation of the volatile constituents is terminated. Nevertheless, these materials are very difficult to classify because the constituents of heavy oils and residua fall into a boiling range in which very little is known about the individual model compounds (Speight, 1999).

Table 3.3. Properties of Tia Juana Crude Oil and Its 650°F, 950°F, and 1050°F Residua (Adapted from Speight, 1999)

	Whole Crude	Residua		
		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

It is even more confusing when an increase in boiling point is directly equated to an increase in the number of rings. Such a system often fails to acknowledge that an increase in boiling point of any ring compound can also (and more likely in the case of petroleum constituents) be equated to an increase in the number or size of the alkyl substituents on the ring.

Another classification method (Burg et al., 1997) involves the use of chromatographic data. This method evaluates the individual interactions that can take place at the molecular level and determines the strength of these interactions. The result is the classification of crude oil on the basis of polarity and relation of polarity to behavior.

The United States has defined tar sands as set forth in the 1976 Federal Energy Administration Ruling (FEA, 1976) that captures the meaning of both tar sand and tar sand bitumen as

... the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques. The hydrocarbon-bearing rocks are variously known as bitumen-rocks oil, impregnated rocks, tar sands, and rock asphalt.

In this definition, the terms must be used in context. For example, removing specific words such as *extremely viscous* or *natural state* does not accomplish anything. The term *extremely viscous* cannot be quantified on its own or out of context and the term *natural state* as it is applied in the definition is interpreted to mean composition. Indeed, it is almost as though the formulators of the definition were looking at the bitumen recovery operations in Canada for guidance insofar as the Canadian bitumen recovery operations defined bitumen. On the other hand, the generic term *heavy oil* is often applied to a petroleum that has an API gravity of less than 20°, and those petroleum materials having an API gravity less than 10° have been referred to as bitumen. Following from this convenient, but questionable, generalization, there has also been an attempt to classify petroleum, heavy oil, and tar sand bitumen using a modified API gravity or viscosity scale.

Use of such a scale would require a fine line of demarcation between the various crude oils, heavy oils, and bitumen to the point where it would be confusing to have to differentiate between a material having a viscosity of 9950 cp and one having a viscosity of 10,050 cp. Furthermore, the inaccuracies (i.e., the limits of experimental error) of the method of measuring viscosity also increase the potential for misclassification. The question of the classification of an oil having a viscosity of 10,000 cp would generate considerable discussion.

The same rationale can be applied to the use of API gravity where the difference between an oil having an API gravity of 9.9° and an oil having an API gravity of 10.1° is very questionable. One also has to wonder how an oil with an API gravity of 10.0° might be classified!

To classify petroleum, heavy oil, and bitumen, the use of a single parameter such as viscosity is not enough. Various other properties, perhaps such as API gravity, viscosity, elemental analysis, composition, and (more appropriately) the properties of the fluid in the reservoir as well as the method of recovery must be acknowledged.

As defined earlier (Chapter 1), bitumen is a naturally occurring material that is found in deposits in which the permeability is low and passage of fluids through the deposits can only be achieved by prior application of fracturing techniques. Tar sand 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. It might also be added that the deposits in which bitumen is found require prior fracturing techniques to overcome the low permeability and allow the passage of fluids.

Any attempt to classify petroleum, heavy oil, and bitumen on the basis of a single property is no longer sufficient to define the nature and properties of petroleum and petroleum-related materials, perhaps being an exercise in futility. Such an attempt would be analogous to classifying the human race on the basis of the physical characteristics of a sumo wrestler, thereby omitting many other anthropological characteristics.

Tar sand bitumen is a naturally occurring material that is immobile in the deposit and cannot be recovered by the application of enhanced oil recovery technologies, including steam-based technologies. On the other hand, heavy oil is more mobile in the reservoir than bitumen and can be recovered by the application of enhanced oil recovery technologies, including steam-based technologies.

The most significant property of bitumen is its *immobility* under the conditions of temperatures and pressure in the deposit. Although the interrelated properties of API gravity (ASTM D-287) and viscosity (ASTM D-445) may present an *indication* of the mobility of oil or immobility of bitumen, these properties offer subjective descriptions of the oil in the reservoir; the most pertinent and objective representation of this oil or bitumen mobility is the *pour point* (ASTM D-97).

In fact, the pour point of an oil, when used in conjunction with the reservoir temperature, gives a better indication of the condition of the oil in the reservoir than the viscosity. Thus the pour point and reservoir temperature present a more accurate assessment of the condition of the oil in the reservoir, being an indicator of the mobility of the oil in the reservoir.

By definition, the *pour point* is the lowest temperature at which oil will move, pour, or flow when it is chilled without disturbance under definite conditions (ASTM D-97).

Most known Canadian tar sand deposits have natural temperatures above the pour point of the bitumen contained therein, and the bitumen has a viscosity in excess of 100,000 cp at reservoir temperatures; the bitumen is plastic to semisolid and is immobile in the deposit.

When used in consideration with reservoir temperature, the pour point gives an indication of the liquidity of the heavy oil or bitumen and, therefore, the ability of the heavy oil or bitumen to flow under reservoir conditions. In summary, the pour point is an important consideration because, for efficient production, additional energy must be supplied to the reservoir by a thermal process to increase the reservoir temperature beyond the pour point.

For example, Athabasca bitumen with a pour point in the range of 50–100°C (122–212°F) and a deposit temperature of 4–10°C (39–50°F) is a solid or near solid in the deposit and will exhibit little or no mobility under deposit conditions. Pour points of 35–60°C (95–140°F) have been recorded for the bitumen in Utah with formation temperatures on the order of 10°C (50°F). This indicates that the bitumen is solid within the deposit and therefore immobile. The injection of steam to raise and maintain the reservoir temperature above the pour point of the bitumen and to enhance bitumen mobility is difficult, in some cases almost impossible.

Conversely, when the reservoir temperature exceeds the pour point the oil is fluid in the reservoir and therefore mobile. The injection of steam to raise and maintain the reservoir temperature above the pour point of the bitumen and to enhance bitumen mobility is possible, and oil recovery can be achieved.

A method that uses the pour point of the oil and the reservoir temperature adds a specific qualification to the term “extremely viscous” as it occurs in the definition

**Table 3.4. Attempted Classification of Bitumen
(Adapted from Speight, 1999)**

Maceral Group	Maceral Subgroup	Maceral
Migrabitumen	Asphaltite Impsonite	Ozocerite Bitumen Gilsonite Glance pitch Grahamite Wurtzilite Albertite Epi-impsonite Meso-impsonite Cata-impsonite

of tar sand. The general applicability of the comparison of the two temperatures shows promise and warrants further consideration.

A recent attempt (Jacob, 1989) has been made to classify migrabitumen (Table 3.4). The term *migrabitumen* signifies a secondary bitumen (or, to use coal terminology, a secondary maceral) that has been generated from fossil organic material during diagenesis and catagenesis (Hunt, 1996). Perhaps this is one of the few subgroups of the petroleum-type materials that can be classified with any degree of accuracy. Their properties are sufficiently different to allow such a classification.

There have also been several attempts to classify kerogen in addition to the general type classification that already exists. However, an interesting set of criteria derived from pyrolysis-gas chromatography (Horsfield, 1984) has shown that hydrocarbon generation can be quantified. It is also interesting to note from this work that hydrogen deficiency in the original kerogen is not directly equated to a low oil-producing propensity. This and other work will not only assist in more accurate descriptions (classification) of kerogen but also offers the potential for a more detailed description of organic facies).

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CHAPTER

4

PHYSICAL PROPERTIES

4.1. INTRODUCTION

Petroleum, heavy oil, and bitumen exhibit a wide range of physical properties, but whereas the properties such as viscosity, density, boiling point, and color of petroleum, heavy oil, and bitumen vary widely, the elemental (ultimate) analysis varies over only a narrow range for a large number of samples. In fact, relative to another fossil energy resource (coal), the carbon content is fairly constant.

The hydrogen and heteroatom contents vary to a greater extent than the carbon content and are often considered to be responsible for the major differences among petroleum, heavy oil, and bitumen. However, this does not take into consideration the relative volatility of the various constituents of these three feedstocks. Nitrogen, oxygen, and sulfur can be present in only trace amounts in some petroleum, which as a result consists primarily of hydrocarbons. In fact, bitumen containing 9.5% by weight heteroatoms may contain very few, if any, true hydrocarbon constituents because as the constituents contain *at least one or more* nitrogen, oxygen, and/or sulfur atoms within the various molecular structures. Coupled with the changes to the feedstock constituents brought about by refinery operations, it is not surprising that petroleum characterization is a monumental task.

Refinery processes can be conveniently divided into three fundamentally different types (Fig. 4.1):

separation: division of the feedstock into various streams (or fractions) depending on the nature of the crude material;

conversion: the production of salable materials from the feedstock by skeletal alteration, or even by alteration of the chemical type of the feedstock constituents; and

finishing: purification of the various product streams by a variety of processes that remove impurities from the product.

In some cases, a fourth category can be added that includes processes such as the *reforming (molecular rearrangement) processes*. For the purposes of this text,

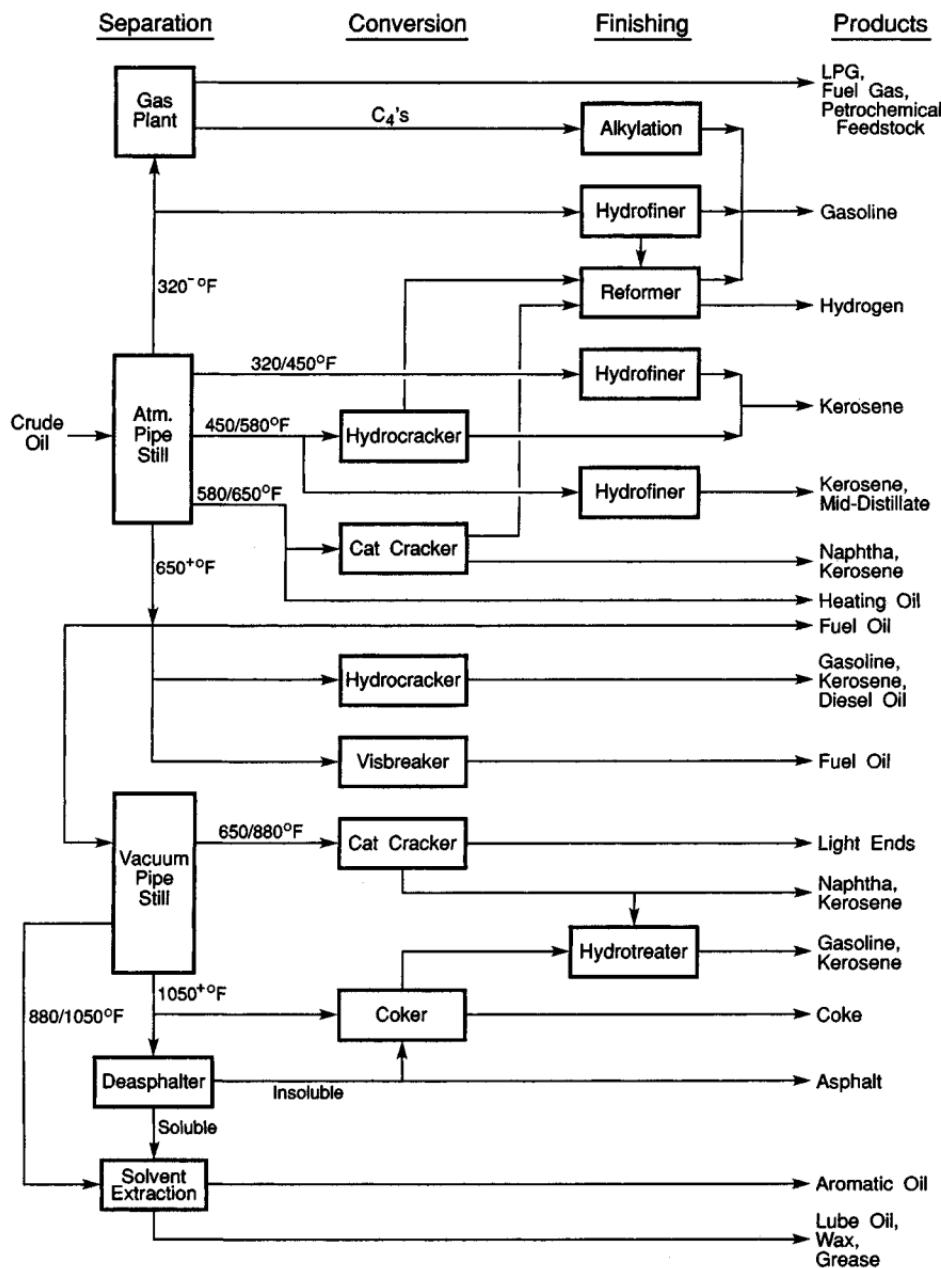


Figure 4.1. Schematic representation of a petroleum refinery (from Speight, 1999).

Table 4.1. Elemental Ratios for Various Fossil Fuels

	Carbon Wt%	Hydrogen Wt%	Nitrogen Wt%	Oxygen Wt%	Sulfur Wt%	H/C Atomic	N/C Atomic	O/C Atomic	S/C Atomic
Crude oil	85.8	13.0	0.2	0.0	1.0	1.818	0.002	0.000	0.004
Qayarah heavy oil (Iraq)	80.7	10.2	0.7	0.0	8.4	1.519	0.007	0.000	0.039
Cold Lake heavy oil (Canada)	83.7	10.4	0.4	1.1	4.4	1.491	0.004	0.010	0.020
Athabasca bitumen (Canada)	83.1	10.3	0.4	1.3	4.9	1.487	0.004	0.012	0.022
Coal									
Anthracite	93.7	2.4	0.9	2.4	0.6	0.307	0.008	0.019	0.002
Bituminous	84.5	5.6	1.6	7.0	1.3	0.795	0.016	0.062	0.006
Lignite	72.7	4.2	1.2	21.3	0.6	0.693	0.014	0.220	0.003

reforming (etc.) processes are included in the finishing processes because that is precisely what they are, processes designed to *finish* various refinery streams and render the products ready for sale.

The analytical chemist attached to a refinery or process research laboratory must be able to respond to the requirements of each of the above process categories through use of a variety of analytical methods that produce data for process predictability and monitoring. The data must be acquired by methods that are quantitatively reproducible and offer a high degree of precision. As a side comment, one must question the value of any method that might be reproducible but only offers accuracy to within 10% above or below the true value; that is, a mean data point that offers 10% variability is of very questionable value.

Although it is possible to classify refinery operations using the general categories outlined above, the behavior of various feedstocks in refinery operations is not simple. The atomic ratios from ultimate analysis (Table 4.1) can give an indication of the nature of a feedstock and the generic hydrogen requirements needed to satisfy the refining chemistry (Speight, 1999). Despite this apparent benefit of knowing the atomic ratios, it is difficult, if not impossible, to predict with any degree of certainty how the feedstock will behave during refining. Any deductions made from data such as the atomic ratios are speculative and are open to much doubt.

The chemical composition of a feedstock is a much truer indicator of refining behavior. Whether the composition is represented in terms of compound types or in terms of generic compound classes, it can offer the refiner a measure of predictability through an understanding of the nature of refinery chemistry. Hence, chemical composition not only plays a large part in determining the nature of the products that arise from the refining operations but also plays a role in determining

the means by which a particular feedstock should be processed (Nelson, 1958; Gary and Handwerk, 1975; Ali et al., 1985; Wallace et al., 1988; Speight, 2000).

In another way, the judicious choice of a crude oil to produce any given product is just as important as the selection of the product for any given purpose. Thus 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. In addition, petroleum evaluation using physical property data is a major part of the initial study of any petroleum destined as a refinery feedstock. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of their significance. In this chapter, an indication of the physical properties that may be applied to petroleum, or even petroleum product, evaluation will be presented.

To satisfy specific needs with regard to the type of petroleum to be processed, as well as to the nature of the product, most refiners have, over time, developed their own methods of petroleum analysis and evaluation. However, such methods are considered proprietary and are not normally available. Consequently, various standards organizations, such as the American Society for Testing and Materials (ASTM, 1998) in North America and the Institute of Petroleum in Britain (IP, 1999), have devoted considerable time and effort to the correlation and standardization of methods for the inspection and evaluation of petroleum and petroleum products. A complete discussion of the large number of routine tests available for petroleum fills an entire book (ASTM, 1998). However, it seems appropriate that in any discussion of the physical properties of petroleum and petroleum products reference be made to the corresponding test, and accordingly the various test numbers have been included in the text.

As indicated elsewhere (Speight, 1999, 2000), petroleum is an exceedingly complex and structured mixture consisting predominantly of hydrocarbons and containing sulfur, nitrogen, oxygen, and metals as minor constituents. As a result of this complexity, the importance of the correct *sampling* of either liquefied petroleum gases (ASTM D-1265) or liquid petroleum (ASTM D-270), heavy oil, and bitumen (Wallace, 1988) cannot be overstressed. Properties such as elemental analysis, metal content, density (specific gravity), and viscosity, to mention only a few properties, are affected by the homogeneity (or heterogeneity) of the sample. In addition, adequate records of the circumstances and conditions during sampling must be made; for example, in sampling from oilfield separators, the temperatures and pressures of the separation plant and the atmospheric temperature would be noted. An accurate sample handling and storage log should be maintained and should include information such as:

1. The precise source of the sample, i.e., the exact geographic location or refinery locale from which the sample was obtained.

2. A description of the means by which the sample was obtained.
3. The protocols that have been used to store the sample.
4. Chemical analyses, such as elemental composition.
5. Physical property analyses, such as API gravity, pour point, distillation profile, etc.
6. The (ASTM) methods used to determine the properties in items 4 and 5.
7. The number of times that the samples have been retrieved from storage to extract a portion, i.e., indications of exposure to the air or oxygen.

Attention to factors such as these enables standardized comparisons to be made when subsequent samples are taken.

However, before this occurs several protocols are involved in initial isolation and clean up of the sample. In fact, considerable importance attaches to the presence of *water* or *sediment* in crude oil (ASTM D-1796, ASTM D-4007) 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 sediment consists of finely divided solids that may be dispersed in the oil or carried in water droplets. The solids 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. In any event, the sediment can lead to serious plugging of the 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. The quantity is generally limited by pipeline companies and by refiners, and steps are normally taken at the wellhead to reduce the water content as low as possible. However, water can be introduced during shipment and, in any form, water and sediment are highly undesirable in a refinery feedstock; the relevant tests (ASTM D-96, ASTM D-954, ASTM D-1796, IP 75) are regarded as important in crude oil quality examinations. Before assay it is sometimes necessary to separate the water from a crude oil sample, and this is usually carried out by one of the procedures described in the preliminary distillation of crude petroleum (IP 24).

Heavy oil and bitumen often form persistent emulsions that are difficult to separate, and in testing wax-bearing crude oils 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. Careful sampling of a crude oil is necessary when examination must be made for suspended impurities of the type discussed.

There is a great variation in the *salt content* of crude oil depending mainly on the source and possibly on the producing wells or zones within a field. In addition, at the refinery, salt water introduced during shipment by tanker may have contributed to this total salt content. These salts have adverse effects on refinery operations especially in increasing maintenance following corrosion in crude units and heat exchangers. It is common practice to monitor wells in a producing field for high salt content, and it is also general practice to desalt the crude at the refinery. The determination of the salt content of crude oil is often made, but as with water and sediment tests, careful sampling is necessary. It would appear that further tests to determine the corrosiveness due to the individual chemical components of the "salt" and also a determination of the extent of evolution of hydrogen chloride on heating would be desirable.

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

In the current context, the evaluation of petroleum, heavy oil, or bitumen for use as a feedstock usually involves an examination of one or more of the physical properties of the material. By this means, a set of basic characteristics can be obtained that can be correlated with utility. The physical properties of petroleum and petroleum products are often equated with those of the hydrocarbons because, although petroleum is indeed a very complex mixture, there is gasoline, produced by nondestructive distillation (straight-run gasoline), in which fewer than a dozen hydrocarbons make up at least 50% of the material (Speight, 1999). However, for the purposes of this chapter, data relating to various physical properties have been included as illustrative examples, but theoretical discussions of the physical properties of hydrocarbons were deemed irrelevant and are omitted.

Over the past three decades, the overall character of the feedstocks entering refineries has changed to such an extent that the difference can be measured by a decrease of several points on the API gravity scale. Consequently, there has been an increasing need for refineries to accept heavy oil and bitumen as part of the refinery feedstock inventory. This has, of course, seen an increase in the need to understand the analytical aspects of these heavier feedstocks. Thus, where possible, information is included here that relates to the properties and processability of heavy oil and bitumen.

4.2. ELEMENTAL (ULTIMATE) ANALYSIS

As already indicated (Chapter 2), the atomic ratios of the elements in various feedstocks have been used as a measure of the general amounts of hydrogen used to convert the feedstock to a given slate of products. In fact, the analysis of petroleum for the percentages of carbon, hydrogen, nitrogen, oxygen, and sulfur is perhaps the first method used to examine the general nature and perform an evaluation of a feedstock. The atomic ratios of the various elements to carbon (i.e., H/C, N/C, O/C, and S/C) are frequently used for indications of the overall character of the feedstock as well as the hydrogen requirements to convert the heteroatoms to their hydrogen analogs (NH_3 , H_2O , H_2S). The H-to-C ratio has been of particular use in the past as a means of estimating the aromaticity of feedstocks. This ratio finds less use now because of the influx of heavier feedstocks into refineries as well as the need for more accurate estimation of feedstock character.

However, elemental analysis is still of considerable value in determining the amounts of elements in feedstocks, especially the trace elements such as vanadium and nickel, because these materials can have serious deleterious effects on catalyst performance during refining by catalytic processes. Indeed, one may wonder about the utility or futility of measuring elements that are present in trace amounts. However, considering the nature of many continuous (as opposed to batch) processes in which a feedstock might be recycled to extinction and blended on the way with fresh feedstock (until no more of the desired product is made), the concentration of the trace elements (metals) on the catalyst can become sufficient to modify, if not completely change, the catalyst's behavior and efficiency.

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

The *ultimate analysis* (elemental composition) of petroleum is not reported to the same extent as that for coal (Speight, 1994). However, of the data that are available, the proportions of the elements in petroleum vary only slightly over narrow limits:

Carbon 83.0–87.0%

Hydrogen 10.0–14.0%

Nitrogen 0.1–2.0%

Oxygen 0.05–1.5%

Sulfur 0.05–6.0%

However, there is a wide variation in physical properties from the lighter, more mobile crude oils at one extreme to the heavier asphaltic crude oils at the other extreme. The majority of the more aromatic species and the heteroatoms occur in the higher-boiling fractions of feedstocks. The heavier feedstocks are relatively rich in these higher-boiling fractions.

The carbon and hydrogen content is often combined with nuclear magnetic resonance data to produce average structures. Some comment on the utility or futility of this aspect of petroleum analysis is made elsewhere (Chapters 11 and 14).

As with coal, there are several ASTM procedures (ASTM, 1998) that can be applied to the ultimate analysis of petroleum and petroleum products, but many such methods may have been designed for other materials. Indeed, some of these methods are used for the elemental analysis of coal.

For example, *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). Indeed, the latter method is also suitable for the determination of carbon and hydrogen in heavy oil and bitumen.

The principles behind carbon and hydrogen analysis have remained relatively unchanged as the methods have become more automated. However, the precision of the analysis of heavy oil, bitumen, and residua may be much poorer than anticipated. This may be related not only to the character of the sample but also to sample size. The use of more controlled combustion conditions as well as the incorporation of corrections for the presence of solids and water are recommended.

Thus 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:

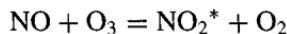
1. *carbon and hydrogen content* (ASTM D-1018, ASTM D-3178, ASTM D-3343, ASTM D-3701, ASTM D-5291, ASTM E-777, IP 338);
2. *nitrogen content* (ASTM D-3179, ASTM D-3228, ASTM D-3431, ASTM E-148, ASTM E-258, ASTM D-5291, and ASTM E-778);
3. *oxygen content* (ASTM E-385), and
4. *sulfur content* (ASTM D-124, 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 fuels and petroleum products from atmospheric distillates to vacuum residua 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 readily in petroleum, with higher amounts usually occurring heavy oil and bitumen. The organically bound nitrogen compounds cause serious problems during upgrading, especially when the levels exceed 0.5% by weight, as happens often in heavy oil and bitumen. Nonaqueous potentiometric titration and other methods have shown that basic nitrogen can be 35% by weight or more of the total nitrogen in petroleum, heavy oil, and bitumen. It is this type of nitrogen that causes poisoning of acidic and metal-containing process catalysts. 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 coke yield.

The determination of nitrogen in petroleum has been 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.

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(ClO₄)₂] before entering the reaction chamber of a chemiluminescence detector. In the detector, ozone reacts with the nitric oxide to form excited nitrogen dioxide:



Photoemission occurs as the excited nitrogen dioxide reverts to the ground state:



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 heavy oil and bitumen. Although the level in well-preserved specimens rarely exceeds 1.5% by weight, it may still be critical to the refiner because of the potential for interaction during refinery processes. In addition, the type of oxygen function in the material

can have an effect on recovery processes. For example, the presence of carboxylic acids ($-CO_2H$) can be beneficial to *in situ* recovery operations by causing a lowering of the interfacial tension (Section 4.6, page 118) between the oil and water. However, such an effect can have serious drawbacks because of the formation of stable oil-in-water emulsions that must be broken at the surface before further processing can occur. In addition, the presence of phenolic ($Ar-OH$) compounds can lead to the formation of polymers and stable ethers ($Ar-O-Ar$) during upgrading that accumulate on catalysts and decrease catalyst activity and efficiency. Guard beds may be necessary to protect the catalyst.

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 (Chapters 8 and 11).

The *total acidity* of a sample or whole feedstock (ASTM D-974, IP 139) is determined for many products, especially fuels, but the method may lack sufficient sensitivity for specific (military) fuels insofar as the detection of trace acidic materials that can affect the water separation from the fuel. Various laboratories have modified this method to accommodate this shortcoming, and there is a more precise acidity test method (IP 273).

Oxygen-containing impurities in the form of *gum* are determined by the *existent gum* test method (ASTM D-382, IP 131) (Chapter 13) and *potential gum* test method (ASTM D-873, IP 138). 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. Functional group analysis (Chapter 8) of the feedstock and the gum adds further valuable information that can lead to steps being taken to mitigate gum formation.

As the third most common element in petroleum, *sulfur* has been analyzed extensively. Analytical methods range from elemental analyses to functional group (sulfur-type) analyses to structural characterization to molecular speciation (Chapter 11).

Of the methods specified for the determination of sulfur (page 92), the method applied to the corrosion effect of sulfur is 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*) that 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 caused by 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 determination of sulfur in liquid petroleum hydrocarbons 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 ^{55}Fe source, fluorescent X rays result. The sulfur $\text{K}\alpha$ fluorescence and a background correction at adjacent wavelengths are counted. A calibration of the instrument, in which 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.

The determination of sulfur with a dedicated X-ray fluorescence analyzer provides a very fast analysis for homogeneous liquid petroleum hydrocarbons. Distillation cuts provide an excellent sample for this method. The method, however, may produce unreliable data for samples that are not homogeneous. For these samples, a gravity separation of the solids occurs during the measurement and gives rise to time-dependent or biased results.

A small matrix effect occurs because of absorption of the sulfur $\text{K}\alpha$ radiation by the sample matrix. The atomic hydrogen-to-carbon ratio and density of the sulfur matrix have both been correlated with this attenuation of X-ray fluorescence, but, in actual practice, matrix effects are minimized by the calibration procedure. Linear calibrations for this procedure have been established up to 6% by weight sulfur. Above this sulfur level, a small bias toward low response may occur and has been attributed to the self-absorption of the sulfur $\text{K}\alpha$ radiation. 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 in petroleum samples 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 triiodide ion to consume the resultant sulfur dioxide. It is intended to distinguish the technique from reductive microcoulometry that converts sulfur in the sample to hydrogen sulfide that is titrated with coulometrically generated silver ion.

The advantages of oxidative microcoulometry include sensitivity, selectivity, speed, linearity of response, and reasonable freedom from interference. The concentration range covered by this method is suitable for many samples in which bitumen upgrading has resulted in considerable desulfurization. The limitation in the sensitivity of the method described here arises from the single inlet that is limited to a maximum sample size of about 5 μL . The injection of larger samples may overload the combustion capacity of the pyrolysis tube. Lower sulfur concentrations can be analyzed by controlling the sample injection rate to permit the combustion of a larger sample volume. The injection rate may be controlled by using the syringe injection technique or by using a controlled rate injector.

Thus the method determines the sulfur content of liquid petroleum hydrocarbons with sulfur contents less than about 0.2 wt% and greater than 20 mg/kg and may be adapted to determine sulfur at higher concentrations.

In this method, samples with high sulfur contents are diluted with toluene and an aliquot is injected into the quartz boat of a single boat inlet and transferred to a combustion tube maintained at 975°C (1785°F). In the presence of an 80% oxygen-20% argon gas flow, the sample is oxidized and the combustion products are swept into a titration cell where the sulfur dioxide component reacts with the triiodide ion of the electrolyte. The triiodide consumed is coulometrically replaced. The current required to replace the triiodide is a measure of the total sulfur present in the sample.

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 the method.

The typical light (conventional) petroleum contains less than 1% by weight sulfur. However, it is the high-sulfur crude oils (>1% by weight sulfur) that represent large reserves. The range of sulfur in petroleum is, of course, attributed to differences in the depositional environment of the original precursors, the distribution of the precursors, as well as the level of maturity. In addition, sulfur can be incorporated into petroleum during migration from the source bed to the reservoir as the liquids pass through sulfur-containing minerals.

The immobility of tar sand bitumen in the deposit often causes anomalous effects in sulfur distribution. For example, gravity effects as the bitumen matures may cause a molecular settling in which the higher-molecular-weight (heavier) fraction of the bitumen (asphaltenes and resins) occurs in increased proportions in deeper parts of the deposit over the proportion of the asphaltenes and resins in the bitumen at shallower depths. Because of the higher proportion of sulfur in these two fractions, the result will be higher proportions of sulfur in the bitumen in the deeper parts of the deposit.

The *sulfur content* of petroleum varies from about 0.1 wt. % to about 3 wt. % for the more conventional crude oils to as much as 5–6% for heavy oil and bitumen. Residua, depending on the sulfur content of the crude oil feedstock, may be of the same order or even have a substantially higher sulfur content. Indeed, the very nature of the distillation process by which residua are produced, that is, removal of distillate without thermal decomposition, dictates that the majority of the sulfur, which is located predominantly in the higher-molecular-weight fractions, be concentrated in the residuum.

Of the ultimate analytical data, more has been made of the *sulfur content* than any other property. For example, the sulfur content (ASTM D-124, D-1552, and D-4294) and the API gravity represent the two properties that have, in the past, had the greatest influence on determining the value of petroleum as a feedstock. Correlations between sulfur content and other properties have been developed for a variety of crude oil, heavy oil, and bitumen (Speight, 1999; Speight, 2000). These correlations illustrate the various interrelationships between the various properties of the feedstocks.

Because of the importance of sulfur measurements and the variety of methods available, it is recommended that certified standards (specifically of heavy oil and bitumen) be used to reduce intra- and interlaboratory errors.

4.3. METAL 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 many upgrading processes adversely, poisoning catalysts in refining and causing deposits in combustion.

Heteroatoms affect every aspect of refining. Sulfur is usually the most concentrated and is fairly easy to remove; many commercial catalysts are available that routinely remove 90% of the sulfur. Nitrogen is more difficult to remove than sulfur, and there are fewer catalysts that are specific for nitrogen. Metals cause particular problems because they poison catalysts used for sulfur and nitrogen removal as

well as other processes such as catalytic cracking. In addition, the levels of nickel and vanadium in petroleum, heavy oil, and bitumen must be considered by the geochemist when the origins of petroleum, heavy oil, and bitumen are considered.

Thus the trace components that are also present in crude oils can produce adverse effects in refining by causing corrosion, by affecting the quality of refined products, or by exerting a deleterious influence on the efficiency of various processing catalysts. This last effect has become of increasing importance because of modern developments in refinery processing.

Heavy oils, residua, and bitumen contain relatively high proportions of *metals* either in the form of salts or as organometallic constituents (such as the metalloporphyrins), which are extremely difficult to remove from the feedstock. Indeed, the nature of the process by which residua are produced virtually dictates that all the metals in the original crude oil are concentrated in the residuum (Speight, 2000). Those metallic constituents that may actually *volatilize* under the distillation conditions and appear in the higher-boiling distillates are the exceptions here. The deleterious effect of metallic constituents on the catalyst is known particularly through their ability to modify the selectivity of zeolite catalysts, thereby causing an increase in the formation of coke at the expense of the more desirable liquid products. Thus serious attempts have been made to develop catalysts that can tolerate a high concentration of metals without serious loss of catalyst activity or catalyst life. However, for the most part, the metals concentrate in the coke formed during thermal processes.

A number of the heavy metals such as nickel, vanadium, copper, and iron can also be effectively bound in large organic molecules characteristic of those found in the asphaltene fraction (pentane- or heptane-insoluble portion of the feedstock) and resins.

Nickel and *vanadium* porphyrins are commonly found and show high thermal stability that allows them to pass through the extraction process into the upgrading process. Porphyrins are the major, but certainly not the only, organometallic complexes present. Metals may simply be entrapped or loosely bound in the very large molecules present in the asphaltenes and resins. Although *iron* is present as organometallic compounds, it occurs mostly in the form of process-accumulated rust or is scrounged from pipelines by the crude oil during shipping and pipelining. Thus one should not be caught up in worrying about the geochemical significance of metal such as iron in crude oil.

Without doubt, these metals are present in petroleum, heavy oil, and bitumen, and because catalysts are used extensively in upgrading and are readily poisoned by such metals, it is important to know the amounts present. Significant levels typically found in heavy oil and bitumen include nickel 20–100 ppm; vanadium 50–250 ppm; and iron 150–1000 ppm.

Vanadium compounds can cause refractory damage in furnaces and adverse effects in glass manufacture, steel failure in turbines, as well as catalyst poisoning

when present in distillate feedstocks. Arsenic and lead are also active catalyst poisons in reforming processes, and the presence of sodium in fuel oils causes failures in furnace brickwork. It is necessary, therefore, for crude oils and distillation unit feedstocks to be examined for the presence of these harmful contaminants and some form of treatment to be devised for reducing their effect during or before processing.

Thus it is important to monitor process streams for metal content for several purposes:

1. to track the degree of potential catalyst poisoning that may occur within the reactor caused by feed metal content;
2. to monitor the degree of catalyst physical or chemical breakdown into the product streams; and
3. to provide one of many indicators of change in the process operation.

The analysis of process stream solids 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 variety 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) measuring metals either directly or as the constituents of combustion ash have been designated to determine metals in petroleum products based on a variety of techniques. At the time of 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 examined for metal species by AA spectroscopy (IP 288, IP 285) or by ICAP spectrometry (ASTM C-1109, ASTM C-1111).

AA provides very high sensitivity but requires careful subsampling, extensive sample preparation, and detailed sample-matrix corrections. XRF requires little in terms of sample preparation but suffers from low sensitivity and the application of major matrix corrections. ICAP spectrometry provides high sensitivity and few matrix corrections, but requires a considerable amount of sample preparation depending on the process stream to be analyzed.

Whenever a technique requires ashing of the sample, one of the issues that arises is the potential loss of volatile nickel and vanadium compounds. Both sulfuric acid and elemental sulfur have been used to prevent loss of these metals. In fact, because of this, a wet ashing method is often preferred over dry ashing (Wallace, 1988).

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 samples is of serious concern.

Very low-level samples such as those typically found in conventional petroleum that may be approaching the lower levels of the parts per billion range are best analyzed using the flameless atomic absorption method. Use of a combination plasma atomic emission-mass spectrometry technique is becoming a more popular analytical method for such samples.

For samples in an aqueous matrix at more moderate levels (0.1–200 ppm), the plasma atomic emission technique is currently the most applicable. Analysis is achieved by monitoring the emission intensity of the element-specific ultraviolet/visible radiation emitted as the sample is aspirated into the highly energetic plasma excitation source. Excitation through air-acetylene or nitrous oxide-acetylene flame sources may also be used for the analysis of the light alkali metals, especially potassium. Absolute concentration levels are determined by comparison with known standards analyzed in a similar matrix. Techniques employing excitation sources such as an arc or spark can also be used effectively for semiquantitative analysis.

Analysis for metals in an organic matrix is most easily accomplished using X-ray fluorescence or neutron activation techniques for quantitative analyses. These particular techniques are also applicable to the direct analyses of oil sand solids. Spark techniques can be used for qualitative analyses. The direct aspiration of metal-containing hydrocarbons into the plasma instrument also provides quantitative information, with the assumption that any particulates present are included in the analyses.

The precision of the analysis depends on the metal itself, the method used, and the standard used for calibration of the instrument. Relative standard deviations range from 1% to more than 20%.

In the ICAP emission spectrometer method, nickel, iron, and vanadium content of gas oil samples in the range from 0.1 mg/kg to 100 mg/kg can be determined. 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.

The ICAP spectrometer is an instrument routinely used for the analysis of the dissolved metal composition of aqueous samples. Solid samples are prepared in such a way (ashing and then fusion) that their final analysis matrix is in the aqueous dissolved form. The analysis of metals in a hydrocarbon matrix, potentially containing solids important to the analysis, is a problem. The ashing of a hydrocarbon sample containing metals (whether in organic complexes, elemental, or inorganic complexes) can lead to analysis errors in that some of the complexes, specifically the organometallic compounds, are in a volatile form at typical ashing temperatures

(700–800°C, 1290–1470°F). The metals in organic complexes tend to originate in the high-molecular-weight hydrocarbons found naturally in the feed or generated in the reactor. The inorganic metal complexes originate naturally in the feed, or from the breakdown of catalyst or the formation of inorganic complexes under the reactor conditions. Without ashing and subsequent fusion, any solids present may not reach the analytical region of the instrument, resulting in analytical errors.

Using the ICAP method for the analysis of nickel, vanadium, and iron 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.

4.4. DENSITY, SPECIFIC GRAVITY, AND API GRAVITY

In the early days of the petroleum refining industry, density and specific gravity data were used to:

1. Indicate crude oil quality.
2. Correlate with aromatic character, naphthenic character, and paraffinic character. The specific gravity is highest for aromatics and lowest for paraffins. The API gravity reverses this relationship.

Thus the *density* and *specific gravity* of crude oil (ASTM D-70, ASTM D-71, ASTM D-287, ASTM D-941, ASTM D-1217, ASTM D-1298, ASTM D-1480, ASTM D-1481, ASTM D-1555, ASTM D-1657, ASTM D-4052, IP 235, IP 160, IP 249, IP 365) are two properties that have found wide use in the industry for preliminary assessment of the character of the crude oil.

In the early years of the petroleum industry, density was the principal specification for petroleum and refinery products; it was used to give a very approximate estimation of the gasoline and (more particularly) the kerosene present in the crude oil. However, the derived relationships between the density of petroleum and its fractional composition were valid only if they were applied to a certain type of petroleum and lost some of their significance when applied to different types of petroleum. Nevertheless, density is still used to give a rough estimation of the nature of petroleum and petroleum products.

Density is defined as the mass of a unit volume of material at a specified temperature and has the dimensions of grams per cubic centimeter (a close approximation to grams per milliliter). Density is measured at a standard temperature, mostly 15.6

or 20°C (60 or 68°F) and is often written in the form of d_4^{20} to indicate that it was measured at 20°C and in pycnometer calibrated with water at 4°C (39°F), i.e., with a medium of density equal to 1.0000. The pycnometer method (ASTM D-70) is also applicable to the broader range of samples covered by that procedure. However, only high-viscosity samples, with density equal to or greater than water, are measured using this method. A densimeter is usually used to measure the density of lighter-than-water samples.

Density and specific gravity (thence the API gravity) can be determined relatively easily but are no longer the means of a *preliminary assay* of the sample and are no longer the guide that they used to be in terms of determining (or estimating) the product slate.

The density or specific gravity of petroleum, petroleum products, heavy oil and bitumen may be measured by means of a hydrometer (ASTM D-287, ASTM D-1298, ASTM D-1657, IP 160), a pycnometer (ASTM D-70, ASTM D-941, ASTM D-1217, ASTM D-1480, and ASTM D-1481), by the displacement method (ASTM D-712), or by means of a digital density meter (ASTM D-4052, IP 365) and a digital density analyzer (ASTM D-5002). Not all of these methods are suitable for measuring the density (or specific gravity) of heavy oil and bitumen, although some methods lend themselves to adaptation. The API gravity of a feedstock (ASTM D-287) is calculated directly from the specific gravity.

The pycnometer method (ASTM D-70, ASTM D-941, ASTM D-1217, ASTM D-1480, ASTM D-1481) for determining density is reliable and precise and requires relatively small test samples. However, because of the time required, other methods such as the hydrometer (ASTM D-1298), the density meter (ASTM D-4052), and the digital density analyzer (ASTM D-5002) are often preferred. However, surface tension effects can affect the displacement method, and the density meter method loses some of its advantage when measuring the density of heavy oil and bitumen.

The pycnometer method (ASTM D-70, ASTM D-941, ASTM D-1217, ASTM D-1480, and ASTM D-1481) is routinely used to measure the density of samples being charged to a distillation flask, where volume charge is needed but the volume is not conveniently measured. The volume may be found by weighing the sample and determining the sample density. It is also used in routine measurements of material properties. It is worthy of note that even a small amount of solids in the sample will influence its measured density. For example, 1% by weight solids in the sample can raise the density by 0.007 g/cm³.

The densimeter method (ASTM D-4052) uses an instrument that measures the total mass of a tube by determining its natural frequency of vibration. This frequency is a function of the dimensions and the elastic properties of the tube and the weight of the tube and contents. Calibration with water and air provides data for the determination of the instrument constraints that allow conversion of the natural frequency of vibration to sample density.

Specific gravity is the ratio of the mass of a volume of a substance to the mass of the same volume of water and is dependent on two temperatures, those at which the masses of the sample and the water are measured. When the water temperature is 4°C (39°F), the specific gravity is equal to the density in the centimeter-gram-second (cgs) system, because the volume of 1 g of water at that temperature is, by definition, 1 ml. Thus the density of water, for example, varies with temperature, and its specific gravity at equal temperatures is always unity. The standard temperatures for a specific gravity in the petroleum industry in North America are 60/60°F (15.6/15.6°C). The specific gravity values of petroleum samples are close to those of density and range from about 0.80 for light paraffinic crude oils to about 0.98 for heavy oil and about 1.00–1.03 for bitumen.

The most accurate method of determining the density or specific gravity of petroleum or a petroleum product is to weigh a known volume in a specific gravity bottle at 15.6°C (60°F). If it is not convenient to carry out the determination at this temperature, a correction may be applied by adding or subtracting 0.00063 per °C (per 1.8°F) for temperatures that are above or below 15.6°C (60°F), respectively.

The most rapid method for determining specific gravity is to use a set of hydrometers (ASTM D-1298). A hydrometer is placed in the petroleum sample at 15.6°C (60°F) and allowed to come to rest. The specific gravity is shown on the scale at the point coincident with the surface of the petroleum.

The use of density or specific gravity has largely been replaced by the API (American Petroleum Institute) gravity as the preferred property. It is one criterion that is used in setting prices for petroleum. In the United States, the API gravity has been used for the classification of a reservoir and the accompanying tax and royalty consequences. This property was derived from the Baumé scale:

$$\text{degrees Baumé} = 140/\text{sp gr at } 60/60^\circ\text{F} - 130$$

However, a considerable number of hydrometers calibrated according to the Baumé scale were found at an early period to be in error by a consistent amount, and this led to the adoption of the equation:

$$\text{degrees API} = 141.5/\text{sp gr at } 60/60^\circ\text{F} - 131.5$$

The specific gravity of petroleum usually ranges from about 0.8 (45.3° API) for the lighter crude oils to over 1.0 (10° API) for heavy crude oils and bitumen (Speight, 1999).

Recently, a scale called the *incremental density* was proposed (Altgelt and Boduszynski, 1994) that is defined by the relationship:

$$D_i = (d - 0.5) (200)$$

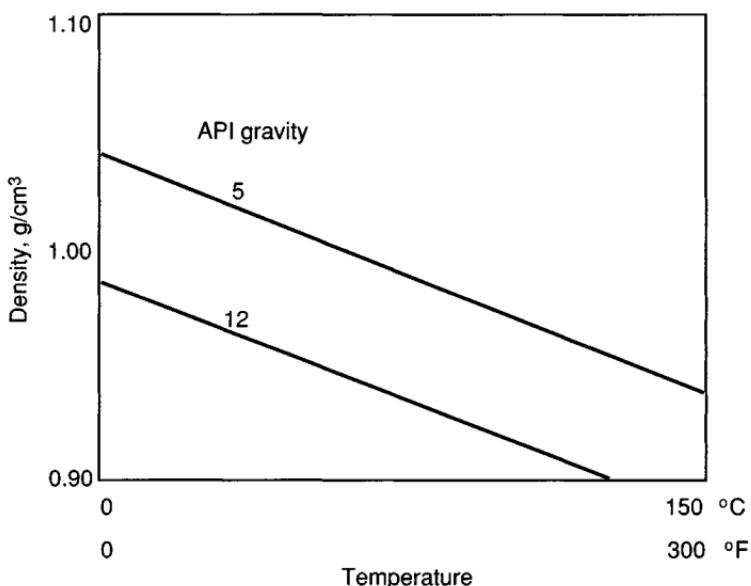


Figure 4.2. Variation of density with temperature.

With this scale, crude oils range from about 60 to 100, which is a span (40 units) similar to the span of the API gravity scale. Whether or not this scale will be accepted for consideration to replace or supplement the API gravity scale, despite the claims of simplicity, remains to be seen. Currently it seems to offer little advantage over the API gravity scale.

The densities of most isocompounds are slightly (but not always) greater than those of the normal hydrocarbons. Ring compounds and heteroatom compounds have a significantly higher density than that of the paraffins. Density, and thus specific gravity, is influenced by the chemical composition of petroleum, but quantitative correlation is difficult to establish, especially when complex mixtures such as petroleum, heavy oil, and bitumen are concerned. However, an interesting aspect of density is its change with temperature (Fig. 4.2), an effect that plays an important role in the recovery of bitumen from tar sand by the hot water process (Speight, 1990).

Thus increased amounts of aromatic compounds result in an increase in density, whereas an increase in saturated compounds results in a decrease in density. Indeed, it is also possible to recognize certain preferred trends between the density of petroleum and one or another of the physical properties. For example, an approximate correlation exists between the density (API gravity) and sulfur content, Conradson carbon residue, viscosity, asphaltenes plus resins, and nitrogen content (Fig. 4.3).

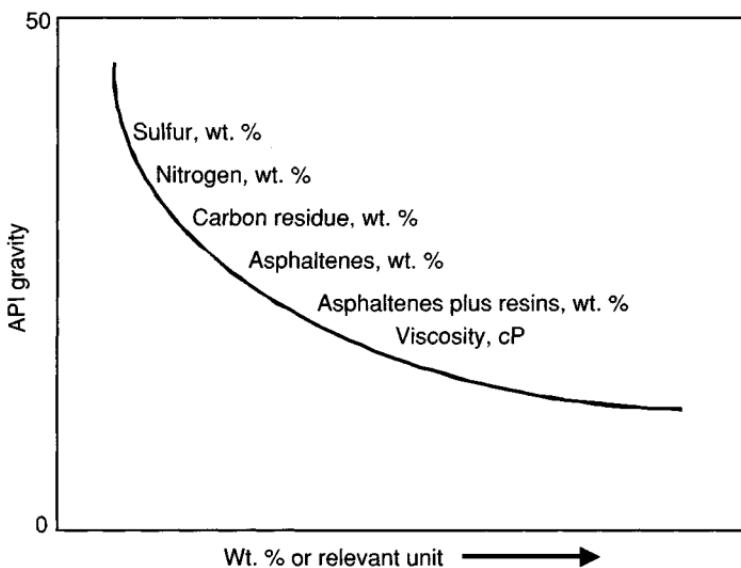


Figure 4.3. Interproperty relationships of various samples.

The variation of density with temperature, effectively the coefficient of expansion, is a property of great technical importance because most petroleum products are sold by volume and specific gravity is usually determined at the prevailing temperature (21°C , 70°F) rather than at the standard temperature (60°F , 15.6°C). The tables of gravity corrections (ASTM D-1555) are based on an assumption that the coefficient of expansion of all petroleum products is a function (at fixed temperatures) of density only. Recent work has focused on the calculation and predictability of density using new mathematical relationships (Gomez, 1989, 1992).

The specific gravity of bitumen shows a fairly wide range of variation. The largest degree of variation is usually caused by local conditions that affect material close to the faces, or exposures, occurring in surface oil sand beds. There are also variations in the specific gravity of the bitumen found in beds that have not been exposed to weathering or other external factors. The range of specific gravity variation is usually of the order of 1.00–1.04 (Table 4.2).

As already noted (page 104), a very important aspect of density (specific gravity) is its variation with temperature (Fig. 4.2), which is also reflected in the variation of the density of Athabasca bitumen with temperature that accounts for the success of the hot water separation process (Speight, 1999, 2000). Over the temperature range of $30\text{--}130^{\circ}\text{C}$ ($85\text{--}265^{\circ}\text{F}$), this variation causes the bitumen to be lighter than water, which has a nonlinear variation of density with temperature. Flotation of the bitumen (with aeration) on the water is facilitated, hence the logic of the hot water separation process (Berkowitz and Speight, 1975; Spragins, 1978).

Table 4.2. Specific Gravity, API Gravity, and Viscosity Data for Bitumen Samples

Source	Specific Gravity	API Gravity	Viscosity	
			cP	°F
Athabasca (Canada)				
Mildred-Ruth Lakes	1.025	6.5	35,000	100
Abasand	1.027	6.3	500,000	100
	1.034	5.4	570,000	100
Ells River	1.008	8.9	25,000	
Utah (United States)				
Asphalt Ridge			610,000	140
Tar Sand Triangle			760,000	140
Sunnyside			1,650,000	100
California				
Arroyo Grande	1.055	2.6	1,300,000	220

However, more detailed studies have been made and the information is available (Wallace, 1988). For example, information is available on density of heavy oil and tar sand bitumen in which the reference temperature used is often 15.6°C (60°F). The precision of the density meter for determining the density of heavy oil and bitumen (ASTM D-4052) tends to suffer because the method was designed for lighter, more conventional petroleum. During the determination of density for heavy oil and bitumen, it may be necessary to heat the sample to lower its viscosity, during which time air bubbles may be trapped in the test sample, giving rise to anomalous results. Dissolving a known mass of sample in a known mass of solvent and injecting the solution into the tube might circumvent this. It is assumed that the volumes of sample and solvent are additive so:

$$\text{mass}_{\text{solution}}/\text{density}_{\text{solution}} = \text{mass}_{\text{sample}}/\text{density}_{\text{sample}} + \text{mass}_{\text{solvent}}/\text{density}_{\text{solvent}}$$

Considerable data exists for the density of heavy oil and bitumen oil found in reservoirs and deposits located in the province of Alberta, Canada (Table 4.2). It must be pointed out that there may be significant differences in the reported densities for bitumen from the same region. For example, bitumen from the extensive Athabasca deposits can range from 0.989 to 1.061. Some of these differences may be bona fide in that the samples could have come from different depths or different parts of the deposit (Schutte, 1974; Speight and Moschopedis, 1981) and the immobility of the bitumen prevents mixing and, therefore, density equilibration. On the other hand, some of the differences may be caused

by the history of the sample. Residual toluene or benzene (or other solvent) as well as oxidation by exposure to air will cause changes in the density as measured.

In addition, the influence of temperature, pressure, and dissolved gases on the density of heavy oil and bitumen from the Cold Lake and Athabasca sources has been reported (Mehrotra and Svrcek, 1981, 1982; Svrcek and Mehrotra, 1982). Similar data have been reported for Athabasca bitumen saturated with carbon dioxide or ethane at higher temperatures and for Cold Lake heavy oil saturated with carbon dioxide (Robinson et al., 1980; Robinson and Sim, 1981). Two additional studies have been reported on the density of Athabasca bitumen to show the effect of pressure, and the second study shows the effect of residual benzene on density (Prowse et al., 1982). The pressure study was done at 15°C, and the residual benzene study was done at 55°C and 1 atmosphere.

The effect of temperature and pressure on the density of bitumen appears to be a general phenomenon because there variations in the density of heavy feedstocks from other parts of the world (Borneo, California, Mexico, and Venezuela) have also been reported (Table 4.3; Pfeiffer, 1950).

An important feature of the inverse of density, the *specific volume*, is the cumulative effect (*additivity*) of atomic contributions. The specific volume is, in reality, the molar volume(MV), which is equal to the density divided by the molecular weight, which is the sum of the atomic volumes. The additivity feature has played an important part in the use of density for average structure determinations. Other features in addition to atomic volumes are needed for the calculation of molar volumes. In alkyl benzenes, and even more so in condensed saturated as well as aromatic ring systems, the junction carbon atoms differ from the regular carbons in their volume contribution.

Finally, density, alone or in combination with other physical properties such as boiling point, has been used for the attempted classification of petroleum and its fractions (Speight, 1999). Examples of such composite parameters include the Watson K factor, also called the UOP K factor, the viscosity gravity constant (VGC), and the refractivity intercept (R_i) (Riazi and Daubert, 1980). For example, a paraffinic hydrocarbon might have a viscosity gravity constant on the order of 0.74–0.75, a Watson factor in the range of 13.1–13.5, and a refractivity intercept of 1.048–1.05. Naphthenic hydrocarbons might have a viscosity gravity constant on the order of 0.89–0.95, a Watson factor in the range of 10.5–13.2, and a refractivity intercept of 1.03–1.046. Aromatic hydrocarbons might have a viscosity gravity constant on the order of 0.95–1.13, a Watson factor in the range of 9.5–12.53, and a refractivity intercept of 1.07–1.105. The precise meaning of such numbers and attempted classification systems remains undefined, especially when the system utilizes (predominantly) a single property (i.e., paraffinic, naphthenic, aromatic) and ranges for complex mixtures such as petroleum heavy oil and bitumen are the norm with overlap between the ranges. In such cases, not only are the accuracy

Table 4.3. Effect of Temperature and Pressure on the Density and API Gravity of Various Residua

Source of residuum	Temperature		Pressure: psi	14.21	2,843	5,685	8,528	11,371	14,214
	°C	°F	Pressure: atm.	0.97	193	387	580	774	967
			Pressure: MPa	0.098	19.6	39.2	58.8	7804	98.0
California	25	77		1.014	1.023	1.031	1.038	1.045	Density, g/cm ³
				8.0	6.8	5.7	4.8	3.9	3.3 API gravity
	45	113		1.002	1.011	1.020	1.028	1.035	1.041 Density, g/cm ³
				9.7	8.5	7.2	6.1	5.2	4.4 API gravity
	65	149		0.990	1.000	1.009	1.017	1.025	1.032 Density, g/cm ³
				11.4	10.0	8.7	7.6	6.6	5.6 API gravity
Venezuela	25	77		1.024	1.032	1.040	1.048	1.054	1.061 Density, g/cm ³
				6.7	5.6	4.6	3.5	2.7	1.9 API gravity
	45	113		1.012	1.020	1.029	1.037	1.044	1.051 Density, g/cm ³
				8.3	7.2	6.0	5.0	4.0	3.1 API gravity
	65	149		1.000	1.009	1.018	1.027	1.034	1.041 Density, g/cm ³
				10.0	8.7	7.5	6.3	5.3	4.4 API gravity

and precision of the analytical method called into question but also the deductive reasoning behind any conclusions.

4.5. VISCOSITY

Viscosity is an important quality of fluid because it is a measure of the internal resistance to motion of a fluid by reason of the forces of cohesion between molecules or molecular groupings. Thus the measurement of the viscosity of petroleum has been regarded by the petroleum industry to have particular importance because of the role it plays in the assessment of petroleum properties and, hence, the producibility of a reservoir. In addition, the viscosity of an oil must also be considered when determining the amount of diluent that will permit pipeline transportation of the oil.

In the early days of the petroleum industry, viscosity was regarded as the *body* of petroleum, a significant number for lubricants or for any liquid pumped or handled in quantity (Speight, 1999). The changes in viscosity with temperature, pressure, and rate of shear are pertinent not only in lubrication but also for such engineering concepts as heat transfer. The viscosity and relative viscosity of different phases, such as gas, liquid oil, and water, are determining influences in producing the flow of reservoir fluids through porous oil-bearing formations. The rate and amount of oil production from a reservoir are often governed by these properties.

Important though it may seem, there are other factors that play a role in the producibility of crude oil from a reservoir. These are reservoir properties such as rock types, permeability, porosity, temperature, and pressure to name only five such factors and without including oil-rock interactions and the role of reservoir water. However, viscosity data are also needed to determine reliable energy requirements for transportation of the produced oils through pipelines.

Viscosity is the force in dynes required to move a plane of 1-cm² area at a distance of 1 cm from another plane of 1-cm² area through a distance of 1 cm in 1 second. In the centimeter-gram-second (cgs) system the unit of viscosity is the poise (P) or centipoise (cP = 0.01 P). Two other terms in common use are *kinematic viscosity* and *fluidity*. The kinematic viscosity is the viscosity in centipoises divided by the specific gravity, and the unit is the stokes (St, cm²/s), although centistoke (cSt = 0.01 St) is in more common usage; fluidity is simply the reciprocal of viscosity.

The viscosity (ASTM D-88, ASTM D-341, ASTM D-445, ASTM D-1270, ASTM D-1665, ASTM D-2161, ASTM D-2170, ASTM D-2171, ASTM D-2270, ASTM D-3205, ASTM D-3570, ASTM E-102, IP 71, IP 212, IP 222, IP 226, IP 319) of crude oils varies markedly over a very wide range. Values vary from less than 10 cP at room temperature to many thousands of centipoises at the same temperature. In the present context, oil sands bitumen occurs at the higher end

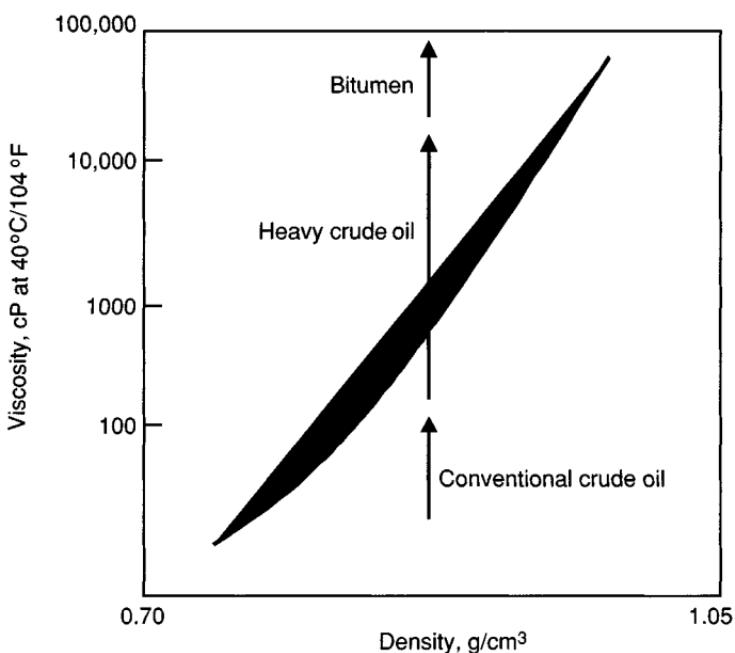


Figure 4.4. Relationship of density and viscosity.

of this scale, where a relationship between viscosity and density between various crude oils has been noted (Fig. 4.4).

Most viscosities are measured with capillary viscometers. Fluids of low and intermediate viscosity are run in viscometers under the driving force of gravity rather than by externally applied pressure. In those cases where the liquid flows by gravity, the kinematic viscosity, η , is measured. The kinematic viscosity is the absolute viscosity (in centipoises) divided by the density, and its unit is the centistoke.

Kinematic viscosity is a measure of the resistive force of a fluid under gravity. Many petroleum products are used as lubricants, and the operation of equipment depends on the proper viscosity of the liquid. Thus the accurate measurement of kinematic viscosity is essential for many product specifications. Also, the kinematic viscosity of many petroleum products is an important parameter for calculating the flow of the liquids through nozzles, orifices, and pipelines.

The time for a volume of liquid to flow through a marked zone in a calibrated glass capillary at a defined temperature is measured and is directly related to the kinematic viscosity. Absolute kinematic viscosity values are obtained through comparison with standards of known viscosity. The Cannon–Fenske method (ASTM D-445) determines the kinematic viscosity of transparent and

opaque petroleum products exhibiting the properties of a Newtonian liquid. The dynamic viscosity can also be calculated if the sample density is known. The kinematic viscosity is reported in units of centistokes to nearest 0.1, and dynamic viscosity is reported in units of centipoises to nearest 0.1.

As noted, the simplest and most widely used viscometers are capillary types (ASTM D-445), and the viscosity (μ) is derived from the equation:

$$\mu = \pi r^4 P / 8nl$$

where r is the tube radius, l the tube length, P the pressure difference between the ends of a capillary, n the coefficient of viscosity, and μ the quantity discharged in unit time. Not only are such capillary instruments the most simple, but when designed in accordance with known principles and used with known necessary correction factors, they are probably the most accurate viscometers available. It is usually more convenient, however, to use relative measurements, and for this purpose the instrument is calibrated with an appropriate standard liquid of known viscosity.

Batch flow times are generally used; in other words, the time required for a fixed amount of sample to flow from a reservoir through a capillary is the datum actually observed. Any features of technique that contribute to longer flow times are usually desirable. Some of the principal capillary viscometers in use are those of Cannon-Fenske, Ubbelohde, Fitzsimmons, and Zeitfuchs.

The Saybolt universal viscosity (SUS) (ASTM D-88) is the time in seconds required for the flow of 60 ml of petroleum from a container, at constant temperature, through a calibrated orifice. The Saybolt furol viscosity (SFS) (ASTM D-88) is determined in a similar manner except that a larger orifice is used.

As a result of the various methods for viscosity determination, it is not surprising that much effort has been spent on interconversion of the several scales (Speight, 1999), especially converting Saybolt to kinematic viscosity (ASTM D-2161),

$$\text{kinematic viscosity} = a \times \text{Saybolt s} + b / \text{Saybolt s}$$

where a and b are constants. There are also tables for converting kinematic viscosity to Saybolt universal viscosity (ASTM D-446) and to Saybolt furol viscosity (ASTM D-666). Standard charts are also available (ASTM D-341) for estimating the viscosity of petroleum or a petroleum product at any temperature provided the viscosity is known at two temperatures.

The Saybolt universal viscosity equivalent to a given kinematic viscosity varies slightly with the temperature at which the determination is made because the temperature of the calibrated receiving flask used in the Saybolt method is not the same as that of the oil. Conversion factors are used to convert kinematic viscosity from 2 to 70 cSt at 38°C (100°F) and 99°C (210°F) to equivalent Saybolt universal viscosity in seconds (Speight, 1999). Appropriate multipliers are listed to

convert kinematic viscosity over 70 cSt. For a kinematic viscosity determined at any other temperature, the equivalent Saybolt universal value is calculated by use of the Saybolt equivalent at 38°C (100°F) and a multiplier that varies with the temperature:

$$\text{Saybolt seconds at } 100^{\circ}\text{F} (38^{\circ}\text{C}) = \text{cSt} \times 4.635$$

$$\text{Saybolt seconds at } 210^{\circ}\text{F} (99^{\circ}\text{C}) = \text{cSt} \times 4.667$$

The Redwood viscometer consists essentially of a standard cylindrical oil cup containing a standard agate orifice at the lower end, into which fits a spherical valve. The oil cup is surrounded by an oil jacket containing a heater and stirring device. The oil in the outer bath is heated 2 or 3° above or below the required temperature of the determination, depending on the relative temperatures of the oil and the surrounding atmosphere. The oil sample, free from solid matter, is heated approximately to the desired temperature and poured into the oil cup up to a standard level. When equilibrium has been reached, i.e., when the oil in the inner cup remains steady at the desired temperature, the oil level is adjusted, the valve is opened, and the time in seconds is taken for 50 ml to run out. This time interval is recorded as the viscosity in Redwood seconds at the specified temperature. The temperature must remain steady during the determination within $\pm 0.25^{\circ}\text{C}$ (0.45°F) for temperatures below 70°C and within $\pm 1^{\circ}\text{C}$ (1.8°F) for temperatures above 70°C (158°F).

U-tube glass viscometers allow an accurately reproducible volume of liquid to pass through a capillary at a constant temperature by the application of an accurately reproducible force. The time taken for a liquid to flow is proportional to the ratio of the dynamic viscosity to the density of the fluid, and hence to its kinematic viscosity. The constant of proportionality for the instrument is obtained by carrying out a determination in the viscometer with a fluid of known viscosity.

The kinematic viscosity of a fluid of viscosity greater than 10 cSt is given by the expression:

$$\nu = Ct$$

where C is the viscometer constant, and t is the time of flow in seconds.

When the fluid has a viscosity of 10 cSt or less, a second coefficient is used to correct for changes in kinetic energy at the exit to the capillary. The expression then becomes:

$$\nu = Ct - B/t$$

where B is the coefficient of kinetic energy, which may be determined experimentally or eliminated by choosing long flow times.

The viscometer constant is determined by use of standard solutions of known kinematic viscosity, e.g., for 4% sucrose $\nu = 4.39$ cSt at 25°C (77°F). Centistokes are still widely used.

To determine viscosity using a U-tube viscometer, a filtered sample of the petroleum or petroleum product under test is introduced into the viscometer by suction or by pipette into the wide tube so that air bubbles are absent and the level of oil stands a few millimeters above the designated level. The viscometer is then placed in a thermostat maintained at the required temperature and adjusted so that it is exactly vertical. After a time, varying from 20 min for temperatures near the normal to 30 min at 100°C (212°F), the samples is blown or sucked into the capillary and then allowed to flow freely back down the capillary, taking the time of fall from a mark to a second mark by means of an accurate stopwatch reading to 1/5 s. The experiment is repeated until duplicate tests are repeatable to $\pm 0.2\%$.

Of the methods available for measuring viscosity, the kinematic viscosity method (ASTM D-445) and the dynamic viscosity method (ASTM D-3205) are the most widely used. From the consideration of precision alone, the kinematic viscosity method is the more accurate for use with bitumen although the reproducibility can range from 10 to 50% (Wallace, 1988). The contribution of sample variability, in the case of an immobile bitumen, is so strong that many samples must be collected and analyzed to hold the variability of the data to 10% at the 95% relative confidence level.

Suitable conversion tables are available (ASTM D-341), and each table or chart is constructed in such a way that for any given petroleum or petroleum product the viscosity-temperature points result in a straight line over the applicable temperature range. Thus, only two viscosity measurements need be made at temperatures far enough apart to determine a line on the appropriate chart from which the approximate viscosity at any other temperature can be read.

The charts can be applicable only to measurements made in the temperature range in which a given petroleum oil is a Newtonian liquid. The oil may cease to be a simple liquid near the cloud point because of the formation of wax particles or near the boiling point because of vaporization. Thus the charts do not give accurate results when either the cloud point or boiling point is approached. However, they are useful over the Newtonian range for estimating the temperature at which an oil attains a desired viscosity. The charts are also convenient for estimating the viscosity of a blend of petroleum liquids at a given temperature when the viscosity of the component liquids at the given temperature is known (Fig. 4.5).

Viscosity decreases with increasing temperature for petroleum or petroleum products. Compared with temperature, viscosity has only a minor influence on viscosity for natural samples. Pressure does play a more important role where dissolved gases are involved because of the dependence of gas solubility on pressure.

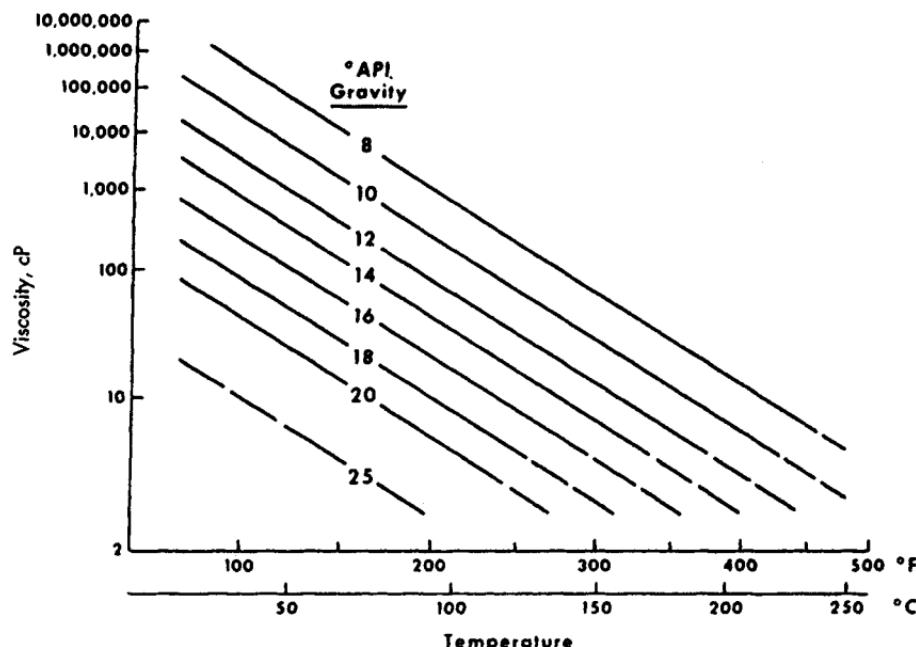


Figure 4.5. Variation of viscosity with temperature.

For lubricants and other petroleum fractions, the ASTM viscosity-temperature chart is the standard method of plotting the viscosity-temperature data for interpolation and extrapolation.

The rate of change appears to depend primarily on the nature or composition of the petroleum, but other factors, such as volatility, may also have a minor effect. The effect of temperature on viscosity is generally represented by the equation

$$\log \log (\nu + c) = A + B \log T$$

where ν is absolute viscosity, T is temperature, and A and B are constants. This equation has been sufficient for most purposes and has come into very general use. The constants A and B vary widely with different oils, but c remains fixed at 0.6 for all oils having a viscosity over 1.5 cSt; it increases only slightly at lower viscosity (0.75 at 0.5 cSt). The viscosity-temperature characteristics of any oil so plotted thus create a straight line, and the parameters A and B are equivalent to the intercept and slope of the line. To express the viscosity and viscosity-temperature characteristics of an oil, the slope and the viscosity at one temperature must be known; the usual practice is to select 38°C (100°F) and 99°C (210°F) as the observation temperatures.

Table 4.4. Variation of Viscosity of Various Athabasca Bitumen Samples with Different Asphaltene Content

Asphaltenes Wt%	Viscosity (80°C, 176°F)	
	MPa·s	cP
10.7	357	357
13.6	270	270
14.6	330	330
14.6	256	256
15.3	521	521
15.7	440	440
16.9	258	258
17.6	438	438
18.1	428	428
18.1	620	620
18.4	655	655
18.8	468	468
18.9	745	745
19.4	744	744
19.7	448	448
20.2	876	876
20.6	498	498
22.9	615	615
25.2	634	634

As with the density (Section 4.4, page 101), the viscosity of petroleum is also related to the asphaltene content (Table 4.4) and increases on the application of pressure. The pressure coefficient of viscosity correlates with the temperature coefficient, even when oil samples of widely different types are compared. A plot of the logarithm of the kinematic viscosity against pressure for several oils has given reasonably linear results up to about 20,000 psi, and the slopes of the isotherms are such that extrapolated values for a given oil intersect. At higher pressures the viscosity decreases with increasing temperature, as at atmospheric pressure; in fact, viscosity changes of small magnitude are usually proportional to density changes, whether these are caused by pressure or by temperature. In summary, an increase in total pressure results in an increase in viscosity of heavy oil and bitumen at any given temperature (Table 4.5). This increase is, however, small compared to viscosity at atmospheric condition.

Because of the importance of viscosity in determining the transport properties of petroleum, recent work has focused on the development of an empirical equation for predicting the dynamic viscosity of low-molecular-weight and high-molecular-weight hydrocarbon vapors at atmospheric pressure (Gomez, 1995). The equation

Table 4.5. Variation of Athabasca Bitumen Viscosity with Temperature and Pressure

Temperature		Pressure			Viscosity	
°C	°F	MPa	atm.	psi	MPa·s	cs
37.8	100	0.093	0.92	13.5	56,658	56,658
93.3	200	0.093	0.92	13.5	397.6	397.6
204.4	400	0.093	0.92	13.5	9.6	9.6
315.6	600	0.093	0.92	13.5	6.8	6.8
37.8	100	0.782	7.7	113	58,447	58,447
93.3	200	0.782	7.7	113	407.5	407.5
204.4	400	0.782	7.7	113	10.4	10.4
37.8	100	1.473	14.2	209	59,640	59,640
93.3	200	1.473	14.2	209	412.5	412.5
204.4	400	1.473	14.2	209	10.9	10.9
315.6	600	1.473	14.2	209	7.0	7.0
37.8	100	2.163	21.4	315	60,634	60,634
93.3	200	2.163	21.4	315	417.5	417.5
204.4	400	2.163	21.4	315	11.4	11.4
315.6	600	2.163	21.4	315	7.2	7.2
37.8	100	2.853	28.2	414	61,628	61,628
93.3	200	2.853	28.2	414	419.5	419.5
204.4	400	2.853	28.2	414	11.9	11.9
315.6	600	2.853	28.2	414	7.4	7.4
37.8	100	3.543	36.1	531	62,622	62,622
93.3	200	3.543	36.1	531	427.4	427.4
204.4	400	3.543	36.1	531	12.4	12.4
315.6	600	3.543	36.1	531	7.4	7.4
210.0	410	8.367	82.6	1,214	8.0	8.0

uses molar mass and specific temperature as the input parameters and offers a means of estimation of the viscosity of a wide range of petroleum fractions. Other work has focused on the prediction of the viscosity of blends of lubricating oils as a means of accurately predicting the viscosity of the blend from the viscosities of the base oil components (Al-Besherah et al., 1989).

Heavy oil and bitumen conform to the oils present in the reservoir in their natural state. Heavy oil may be produced by enhanced recovery processes essentially free of the sand particulates within which the oil resides in the reservoir, but bitumen is normally produced through some form of extraction process, either thermal or solvent-supported, that separates the oil from the sand.

It is very necessary to comment at this point about the role of sample history on the viscosity data. This is particularly important for bitumen. To make fair

comparisons between data obtained on feedstocks from the same geographical location, it is important to ascertain that the bitumen samples have undergone similar extraction and/or storage procedures. The amount of residual fluids in a batch of extracted stock, the period of exposure to air or oxygen, exposure to elevated temperatures, and/or subatmospheric pressures can all significantly alter the absolute viscosity measurements of the bitumen sample. Indeed, reproduction of residual solvent and storage details between feedstocks used by different investigators is often difficult to achieve. This is brought about, in part, by the lack of attention paid toward recording the precise history of a bitumen sample before it is used for measurement of experimental data.

Samples of bitumen from Canada have received considerable attention, especially samples for the various bitumen deposits and heavy oil reservoirs. For example, viscosity measurements on produced samples of Peace River bitumen were carried out to determine the effects of temperature on alteration of asphaltenes in the bitumen, and consequently viscosity measurements were correlated against the asphaltene concentrations of the samples as produced (Table 4.4; Waxman et al., 1980).

The amount of data available for samples from the Wabasca (Alberta, Canada) deposit is quite limited. A range covering 400 to 27,100 cP at 24°C (75°F) and 50 to 700 cP at 65°C (149°F) was reported (Prowse et al., 1982), but sample histories were not given. Viscosity data have also been reported for seven different samples as a function of temperature (Patel, 1973).

Subjecting a sample of bitumen to continuous heating in air at about 100°C (212°F) for 4 days, one author (Jacobs, 1978) observed a substantial increase in viscosity, thereby illustrating the effect of oxidation on the viscosity of bitumen.

A study (Patel, 1973) of the viscosity of 10 samples of bitumen obtained from the Athabasca deposit at different depths shows a general trend of higher bitumen viscosity for samples closer to the surface. In addition, the data also indicate that higher amounts of residual solvent reduce the viscosity, but attempts to remove the last traces cause a depletion of light ends from the oil, thus making it more viscous. This certainly reiterates the need for standardizing the procedures for extracting oil from oil sands as pointed out in the early days of the study of bitumen viscosity (Ward and Clark, 1950).

In fact, first efforts to use controlled experiments to measure bitumen viscosity involved the use of a somewhat laborious, but necessary, procedure for benzene extraction of bitumen from oil sands with the aim of developing a standardized method (Ward and Clark, 1950). It was recognized that it is virtually impossible to extract the bitumen and restore it to the condition in which it existed in the original sand. This accentuated the need to define sample history explicitly.

Studies of the viscosities of samples obtained from several geographic locations in the Athabasca deposit (Ward and Clark, 1950) indicate that the viscosity of bitumen can change within a deposit; in this case the viscosity of the bitumen

samples decreased through the entire deposit from the south to the northern regions. Thus viscosity measurements on samples taken from Abasand in the south were considerably higher than the measurements made on samples from the Bitumount and Ells River regions located north of the Abasand region.

A number of correlations for the variation of viscosity of petroleum with temperature have appeared over the last 50 years. However, in all cases the correlations have been explicitly defined by fitting known data. The constants determined thereby are applicable within the range of temperature and pressure on which the data were available and in addition, are applicable only for the specific oil for which data were obtained. Attempts have also been made to obtain viscosity correlations based on structural and physical property information of liquids so that they may be used to predict viscosities for systems in which no experimental data are available. Such correlations include those based on group contribution methods and on the theory of corresponding states (Reid, et al., 1977).

The classification of lubricating oil by viscosity is a matter of some importance. A useful system is that of the Society of Automotive Engineers (SAE). Each oil class carries an index designation (Speight, 1999). For those classes designated by letter and number, maximum viscosity and minimum viscosity are specified at -18°C (0°F); those designated by number only are specified in viscosity at 99°C (210°F). Viscosity is also used in specifying several grades of fuel oils and in setting the requirement for kerosene and insulating oil.

Because the viscosity-temperature coefficient of lubricating oil is an important expression of its suitability, a convenient number to express this property is very useful, and hence, a viscosity index (ASTM D-567; ASTM D-2270, IP 226) was derived. It is established that naphthenic oils have higher viscosity-temperature coefficients than do paraffinic oils at equal viscosity and temperatures. The Dean and Davis scale was based on the assignment of a zero value to a typical naphthenic crude oil and a value of 100 to a typical paraffinic crude oil; intermediate oils were rated by the formula:

$$\text{viscosity index} = (L - U/L - H) \times 100$$

where L and H are the viscosities of the zero and 100 index reference oils, both having the same viscosity at 99°C (210°F), and U is that of the unknown, all at 38°C (100°F). Originally the viscosity index was calculated from Saybolt viscosity data, but subsequently figures were provided for kinematic viscosity.

4.6. SURFACE AND INTERFACIAL TENSION

Surface tension is a measure of the force acting at a boundary between two phases. If the boundary is between a liquid and a solid or between a liquid and a gas (air)

the attractive forces are referred to as surface tension, but the attractive forces between two immiscible liquids are referred to as *interfacial tension*.

The surface and interfacial tensions of petroleum are important because they are indicative of the ease of formation and stability of emulsions and foams, that is, they indicate the relative *detergent properties* of a crude oil. Thus surface and interfacial tension data can also be used to indicate the potential for oil recovery from a reservoir.

The surface and interfacial tensions are determined by measuring the force necessary to detach a planar ring of platinum-iridium wire from the surface of the liquid. For interfacial tension, the ring is detached from the liquid of higher surface tension. The force is measured by a direct-reading torsion-type balance. This reading is corrected by a factor that depends on the force applied, the density of the solutions, and the dimensions of the ring.

Surface and interfacial tensions provide information pertaining to the presence and concentration of surface-active agents. These compounds play an important role in the performance of flotation and emulsion systems.

The surface tension of a liquid may be measured by a variety of methods. The present procedure is based on the Du Nouy torsion ring method. Because the surface tension affects the equilibrium shape of liquid surfaces, analysis of drop or bubble shapes may also be used to determine surface tension. In addition, the rise of liquid in a capillary may be determined and used to calculate the surface tension quite rapidly.

The (Du Nouy) ring method for measuring surface tension (ASTM D-971) measures the surface tension of both organic and aqueous solutions and the interfacial tension of organic/aqueous phases. A technique for deriving the surface tension of bitumen at ambient temperature is also described.

A general equation (Nelson, 1958, p. 203) for the variation of the surface tension of hydrocarbons with temperature is:

$$V_2 = V_1 [(T_c - T_2)/(T_c - T_1)]^{1.2}$$

in which T is the absolute temperature (degrees Rankine), T_c is the absolute critical temperature, and V is the surface tension in dynes per centimeter. However, the problem in applying this equation to complex systems such as crude oil, heavy oil, and bitumen is the use of critical property data that are not always (in fact, rarely) available. Nevertheless, the equation does offer some basic relationships that can be used for products that contain known hydrocarbon constituents.

In addition, to temperature, molecular weight also has a significant effect on surface tension (Table 4.6). For example, in the normal hydrocarbon series, a rise in temperature leads to a decrease in the surface tension, but an increase in molecular weight increases the surface tension. A similar trend, that is, an increase

Table 4.6. Surface Tension of Selected Liquid Hydrocarbons

Hydrocarbon	°C °F	Surface Tension			
		20 68	38 100	93 200	
<i>n</i> -Pentane	16.0	14.0	8.0	dyn/cm	
	16.0	14.0	8.0	mN/m	
<i>n</i> -Hexane	18.4	16.5	10.9	dyn/cm	
	18.4	16.5	10.9	mN/m	
<i>n</i> -Heptane	20.3	18.6	13.1	dyn/cm	
	20.3	18.6	13.1	mN/m	
<i>n</i> -Octane	21.8	20.2	14.9	dyn/cm	
	21.8	20.2	14.9	mN/m	
Cyclopentane	22.4			dyn/cm	
	22.4			mN/m	
Cyclohexane	25.0			dyn/cm	
	25.0			mN/m	
Tetralin	35.2			dyn/cm	
	35.2			mN/m	
Decalin	29.9			dyn/cm	
	29.9			mN/m	
Benzene	28.8			dyn/cm	
	28.8			mN/m	
Toluene	28.5			dyn/cm	
	28.5			mN/m	
Ethylbenzene	29.0			dyn/cm	
	29.0			mN/m	
<i>n</i> -Butylbenzene	29.2			dyn/cm	
	29.2			mN/m	

in molecular weight causing an increase in surface tension, also occurs in the alicyclic series and, to a lesser extent, in the alkylbenzene series.

The surface tension of petroleum and petroleum products has been studied for many years. There is a narrow range of values (~24–38 dyn/cm) for such widely diverse materials as gasoline (26 dyn/cm), kerosene (30 dyn/cm), and the lubricating fractions (34 dyn/cm), and the surface tension of bitumen (~35 dyn/cm at 21°C, 70°F) is at the higher end of this range. This is somewhat higher than the general value (~30 dyn/cm) found for crude oil. It is, however, not unexpected because generally the surface tension is higher for more viscous crude oil of higher specific gravity. For bitumen, the temperature coefficient from 38°C to 93°C (100–200°F) is approximately –0.153 dyn/cm per °C (–0.085 dyn/cm per °F) (AOSTRAL, 1987).

The range of values for the surface tension is of little value for any attempted characterization or classification of crude oil.

However, it is generally acknowledged that nonhydrocarbon materials dissolved in an oil reduce the surface tension; polar compounds, such as soaps and fatty acids, are particularly active. The effect is marked at low concentrations up to a critical value beyond which further additions cause little change; the critical value corresponds closely with that required for a monomolecular layer on the exposed surface, where it is adsorbed and accounts for the lowering. Recent work has focused on the predictability of surface tension using mathematical relationships(Gomez, 1987):

$$\text{dynamic surface tension} = 681.3/K (1 - T/13.488^{1.7654} \times \text{sg}^{2.1250})^{1.2056}$$

where K is the Watson characterization factor (Chapter 3), sg is the specific gravity and T is the temperature in degrees Kelvin.

A high proportion of the complex phenomena shown by emulsions and foams can be traced to these induced surface tension effects. Dissolved gases, even hydrocarbon gases, lower the surface tension of oils, but the effects are less dramatic and the changes probably result from dilution. The matter is presumably of some importance in petroleum production engineering, in which the viscosity and surface tension of the reservoir fluid may govern the amount of oil recovered under certain conditions.

On the other hand, although petroleum products show little variation in surface tension, within a narrow range the *interfacial tension* of petroleum, and especially of petroleum products, against aqueous solutions provides valuable information (ASTM D-971). Thus the interfacial tension of petroleum is subject to the same constraints as surface tension, that is, differences in composition, molecular weight, and so on. When oil-water systems are involved, the pH of the aqueous phase influences the tension at the interface; the change is small for highly refined oils, but increasing pH causes a rapid decrease for poorly refined, contaminated, or slightly oxidized oils.

A change in interfacial tension between oil and alkaline water has been proposed as an index for following the refining or deterioration of certain products, such as turbine and insulating oils. When surface or interfacial tensions are lowered by the presence of solutes, which tend to concentrate on the surface, some time is required to obtain the final concentration and hence the final value of the tension. In such systems, dynamic and static tension must be distinguished. The dynamic tension concerns the freshly exposed surface having nearly the same composition as the body of the liquid; it usually has a value only slightly less than that of the pure solvent. The static tension is that existing after equilibrium concentrations have been reached at the surface.

The interfacial tension between petroleum and distilled water provides an indication of compounds in the petroleum oil that have an affinity for water. The measurement of interfacial tension has received special attention because of its possible use in predicting when an oil in constant use will reach the limit of its serviceability. This interest is based on the fact that oxidation decreases the interfacial tension of the oil. Furthermore, the interfacial tension of turbine oil against water is lowered by the presence of oxidation products, impurities from the air or rust particles, and certain antirust compounds intentionally blended in the oil. Thus a depletion of the antirust additive may cause an increase in interfacial tension, whereas the formation of oxidation products or contamination with dust and rust lowers the interfacial tension.

In following the performance of oil in service, a decrease in interfacial tension indicates oxidation, if it is known that antirust additives and contamination with dust and rust are absent. In the absence of contamination and oxidation products, an increase in interfacial tension indicates a depletion trend in the antirust additive. Very minor changes over appreciable periods of time signify satisfactory operating conditions. The addition of makeup oil to a system introduces further complications in following the effects of service on the interfacial tension of a particular charge of oil.

The surface tension of heavy oil and bitumen and the interfacial tension of heavy oil and bitumen oils with water may be markedly affected by the presence of dissolved salts or other solutes and by the presence of even very small quantities of surface-active agents. In fact, the issues related to producing reliable and consistent interfacial tension measurements are compounded by the fact that many surface-active agents are indigenous to the oils themselves.

Surface tension measurements by the ring method carried out on heavy oil or bitumen below 60°C (140°F) are inaccurate because of the viscous nature of bitumen. This problem is overcome by measuring the surface tension of several solvent solutions at the desired temperature and extrapolating the resulting linear curve to the whole heavy oil or bitumen. The solvent is usually toluene.

The surface tension of Athabasca bitumen in air and the interfacial tension of pure water with bitumen have been studied (Bowman, 1967; Speight and Moschopedis, 1980). The effect of temperature on the surface tension of Athabasca bitumen is reflected in a reduction in surface tension with an increase in temperature (Table 4.7). Temperature also causes a reduction in the interfacial tension between water and Athabasca bitumen whereas the influence of pH changes brought on by the addition of silica (SiO_2) and sodium oxide (Na_2O) also brings about a decrease of the surface tension of the bitumen-water interface.

Surface tension data and interfacial tension data have been reported for 15° API Lloydminster heavy oil using a ring tensiometer. Interfacial tension was measured distilled water and for field waters taken from the formation. The field waters from

Table 4.7. Effect of Temperature on the Surface Tension of Athabasca Bitumen

Temperature		Surface Tension	
°C	°F	dyn/cm	mN/m
21.1	70.0	35.3	35.3
23.3	74.0	34.7	34.7
30.0	86.0	30.1	30.1
43.3	110.0	27.3	27.3
51.7	125.0	28.0	28.0
65.6	150.0	25.4	25.4
73.9	165.0	22.5	22.5
82.2	180.0	21.0	21.0
87.8	190.0	18.9	18.9
95.6	204.0	20.0	20.0
104.0	219.0	19.2	19.2
123.9	255.0	18.2	18.2

this formation had 73,218 ppm solids of which 67,400 ppm was sodium chloride. The pH was 7.56 at 24.8°C. Thus:

surface tension: 31.7 dyn/cm (mN/m) at 22.8°C

interfacial tension: 20.4 dyn/cm (mN/m) at 25.6°C

Interfacial tension measurements between distilled water and the Lloydminster oil were made over a range of temperatures.

A limited number of data are available for bitumen from Venezuela, Mexico, and Borneo (Pfeiffer, 1950):

Source	Surface Tension, dyn/cm (mN/m)		
	100°C	120°C	150°C
Venezuela	28.8	27.7	26.0
Mexico	29.4	28.1	26.2
	28.7	27.4	25.5
Borneo	30.0	28.8	26.9

The data, like the data for viscosity, tend to show a linear variation with temperature.

Generally, the interfacial tension for crude oil falls in the range 13.6–34.3 dyn/cm at 21°C (70°F), and the interfacial tension is generally higher for paraffinic crude oil. Heavy oil and bitumen containing appreciable quantities of aromatic constituents, naphthenes, and polar species is at the lower end of the range.

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CHAPTER

5

THERMAL PROPERTIES

5.1. INTRODUCTION

As indicated elsewhere (Chapter 2), petroleum is an exceedingly complex and structured mixture consisting predominantly of hydrocarbons and containing sulfur, nitrogen, oxygen, and metals as minor constituents. Although sulfur has been reported in elemental form in some crude oils, most of the minor constituents occur in combination with carbon and hydrogen.

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

Evaluation of petroleum for use as a feedstock involves an examination of several of the physical properties of the material. It is no longer sufficient to use one property only for evaluation purposes. Indeed, the slate of properties required to produce evaluation data may vary from the more convenient physical inspections (Chapter 4) to the more complex physical properties, of which some are described in this chapter. By this means, a set of basic characteristics can be obtained that can be correlated with utility.

Thus, for the purposes of this chapter, the tests that produce data relating to the various thermal properties of petroleum, heavy oil, and bitumen are described. It is these properties that provide valuable information relating to the movement of feedstocks around a refinery as well as indications of the yields of various products.

5.2. VOLATILITY

The volatility of a liquid or liquefied gas may be defined as its tendency to vaporize, that is, to change from the liquid to the vapor or gaseous state. Because one of the three essentials for combustion in a flame is that the fuel be in the gaseous state,

volatility is a primary characteristic of liquid fuels. The distillation profile is also a measure of the relative amounts of these liquid fuels (albeit unrefined) in a crude oil.

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 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.

Similarly, there must also be some estimate of the ability of the constituents of petroleum to distill from the mixture if refining is to be achieved in the most effective manner. The distillation of crude oil has been a method of refining since the beginning of the modern refining industry. The production of kerosene and then the production of gasoline by distillation were integral (sometimes the only) parts of the early methods of refining. Thus the volatility of crude oil in terms of the amounts of the constituents' boiling fractions became a very prominent test for crude oil quality.

However, before any volatility tests are carried out it must be recognized that the presence of more than 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 a real potential for destruction of the glass equipment. Steam formed during distillation can act as a carrier gas and high-boiling-point components may end up in the distillate (often referred to as *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 of the hydrocarbon that codistills with the water into the sample (see also IP 74); and
5. separation of the water from the hydrocarbon distillate by freezing.

The vaporizing tendencies of petroleum and petroleum products are the basis for the general characterization of liquid petroleum fuels, such as liquefied petroleum gas, natural gasoline, motor and aviation gasoline, naphtha, kerosene, gas oil, diesel fuel, and fuel oil (ASTM D-2715). A test (ASTM D-6; see also IP 45) also exists for determining the loss of material when crude oil and asphaltic compounds are

heated. Another test (ASTM D-20) is a method for the distillation of road tars that might also be applied to estimating the volatility of unknown high-molecular-weight residues.

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 and fire, vapor pressure, and evaporation methods are available. The data from the early stages of the several distillation methods are also useful. For other uses, it is important to know the tendency of a product to partially vaporize or to completely vaporize and, in some cases, to know whether small quantities of high-boiling components are present. For such purposes, the chief reliance is placed on the distillation methods.

The *flash point* of petroleum or a petroleum product is the 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 momentarily by a specified flame (ASTM D-56, ASTM D-92, ASTM D-93, ASTM D-1310, ASTM D-3828, IP 34, IP 36, IP 170, IP 303, IP 304, IP 403, 404).

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, and the Abel apparatus (IP 170) is used for more volatile oils with flash points below 50°C. 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 temperature of the oil in the cup is raised at 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 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.

The *open flash point* is determined after the closed flash point by removing the cover and continuing the heating until a distinct flash occurs across the open cup.

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 < 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°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.

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).

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.

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.

A further aspect of volatility that receives considerable attention is the vapor pressure of petroleum and its constituent fractions. The *vapor pressure* 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 exerted on the liquid to prevent it from vaporizing further (ASTM D-323, IP 69). The vapor pressure increases with temperature for any given gasoline, liquefied petroleum gas, or other product. The temperature at which the vapor pressure of a liquid, either a pure compound or a mixture of many compounds, equals 1 atmosphere of pressure (14.7 psi, absolute) is designated as the boiling point of the liquid.

The *Reid vapor pressure* (ASTM D-323, IP 69, IP 402) is a measure of the vapor pressure of petroleum or a petroleum product 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.

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

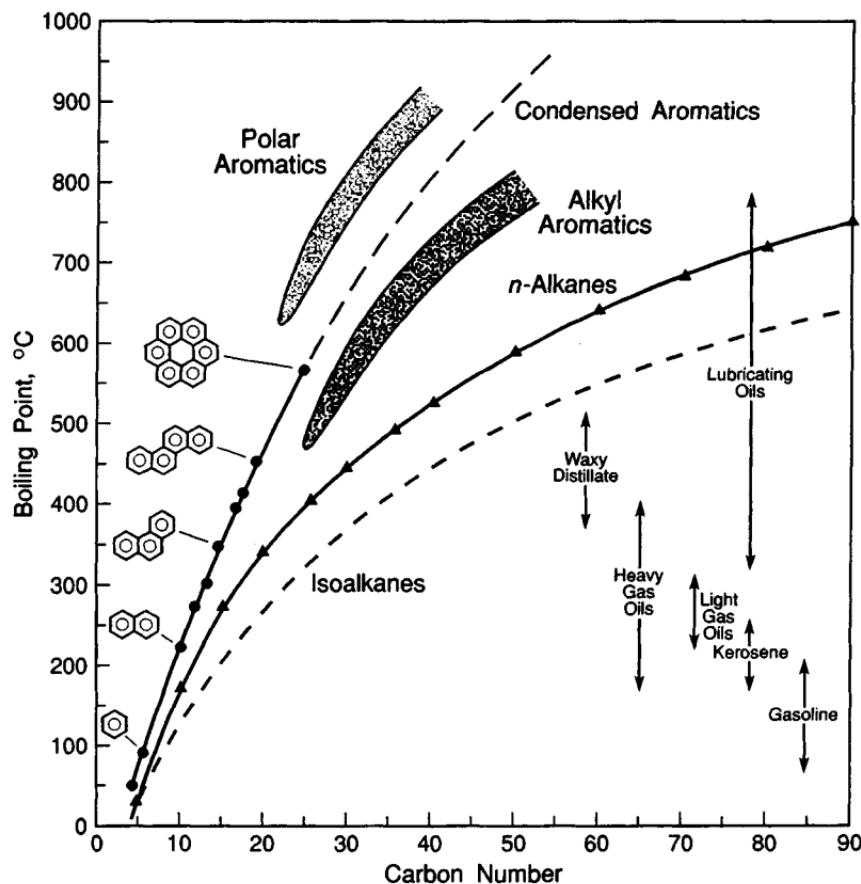


Figure 5.1. Relationship of boiling point to carbon number (from Speight, 1999).

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 asphaltene constituents (Chapters 11 and 14).

The *boiling points* of petroleum fractions are rarely, if ever, distinct temperatures; 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. In general, the limiting molecular weight range for distillation at atmospheric pressure without

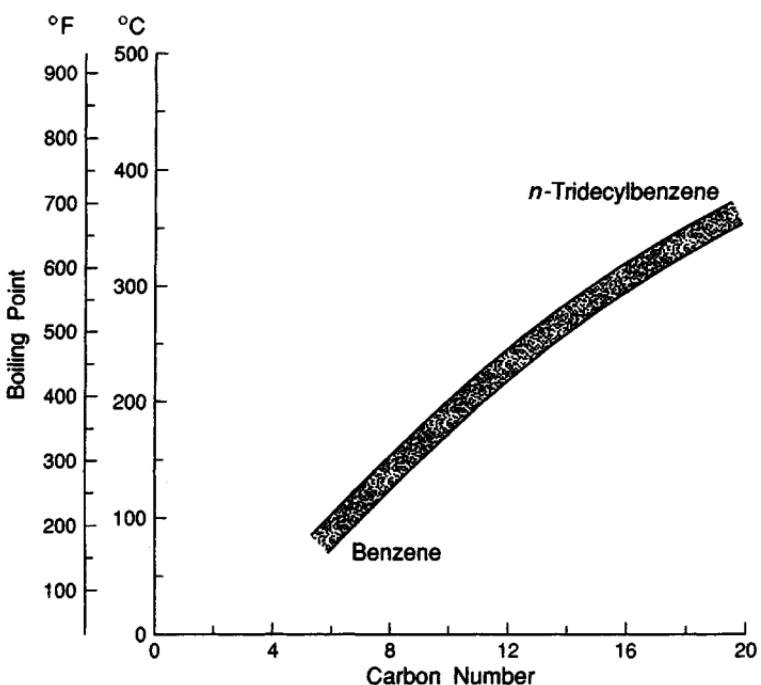


Figure 5.2. Effect of alkyl chain length on boiling point (from Speight, 1999).

thermal degradation is 200–250, whereas the limiting molecular weight range for conventional vacuum distillation is 500–600.

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

- ASTM D-86 (IP 123) - Distillation of Petroleum Products;
- ASTM D-216 (IP 191) - Distillation of Natural Gasoline;
- ASTM D-285 - Distillation of Crude Petroleum;
- ASTM D-1160 - Distillation of Petroleum Products at Reduced Pressure;
- ASTM D-2887 - Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography; and
- ASTM D 2892 - Distillation of Crude Petroleum (15 Theoretical Plate Column).

In fact, distillation was at one time the predominant method by which petroleum feedstocks were evaluated as suitable for various refinery options. It is now one of several methods used for evaluation purposes.

As an early part of characterization studies, a correlation was observed between the quality of petroleum products and their hydrogen content because gasoline, kerosene, diesel fuel, and lubricating oil are made up of hydrocarbon constituents containing high proportions of hydrogen. Thus it is not surprising that the 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.

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 D-447, ASTM D-2892, IP 24, IP 123, IP 191) or at *reduced pressure* (ASTM D-1160). There are also test methods for the distillation of pitch (ASTM D-2569) and cutback asphalt (ASTM D-402) that can be applied to heavy oil and bitumen. However, most of the methods specify an upper atmospheric equivalent temperature (AET) limit of 360°C (680°F) and therefore are too limited to be of value in the analysis of tar sand bitumen.

In the simplest case, the distillation method involves using 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 additional 10 ml distills and the final boiling point are also recorded.

The four distillation procedures that are commonly used by laboratories, either singly or in combination, to determine the distillation curve or produce fractions from heavy oil and bitumen are:

1. ASTM D-2892: Distillation of Crude Petroleum (15 Theoretical-Plate Column).
2. ASTM D-1160: Distillation of Petroleum Products at Reduced Pressures.
3. ASTM D-5236: Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method).
4. Spinning band distillation.
5. Distillation using a flash still.

The ASTM D-2892 method describes the procedure for distilling crude petroleum up to 400°C (752°F) AET. This method is often referred to as the *true boiling point distillation* method.

Crude oil 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 mm Hg, 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*.

The ASTM D-1160 method is used to determine the boiling ranges of petroleum products to a maximum liquid temperature of 400°C (752°F) at pressures as low as 1 mm Hg. 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.

Because of the thermal sensitivity of residua, heavy oils, and bitumen, cracking will most likely occur before the liquid temperature reaches 400°C (752°F). An increase in distillation rate accompanied by a drop in head temperature, loss of vacuum in the system that is restored when heat to the still is reduced, and production of vapor clouds in the system are all evidence of cracking.

The *vacuum potstill method* (ASTM D-5236) is a procedure for the distillation of high-boiling samples with initial boiling points above 150°C (300°F). This includes heavy crude oil, tar sand bitumen, and residua. The method uses a potstill with a low-pressure drop entrainment separator. The method also provides for the determination of standard distillation profiles to the highest AET possible by conventional distillation.

In the *spinning band* method (Fig. 5.3), fractions of feedstocks such as residua, heavy oils, and bitumen with an initial boiling point above room temperature at atmospheric pressure can be prepared. For such materials, the initial boiling point of the sample should exceed room temperature at atmospheric pressure. The distillation is terminated at an AET of 524°C (975°F). For bitumen samples the distillation is terminated at a pot temperature of 360°C (680°F).

Samples are distilled under atmospheric and reduced pressures of 20.0 and 0.60 mmHg (2.67 kPa and 80 Pa) in a distillation unit equipped with a spinning band column. 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 (that is convertible to AET) and distillate volume (that 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.

When fractionating bitumen, the pot temperature cannot exceed 360°C (680°F). In this method, samples are distilled under atmospheric and reduced pressures in a still equipped with a spinning band column. Vapor temperatures are converted to AETs and can be plotted as a function of volume or weight percent distilled to yield a distillation profile.

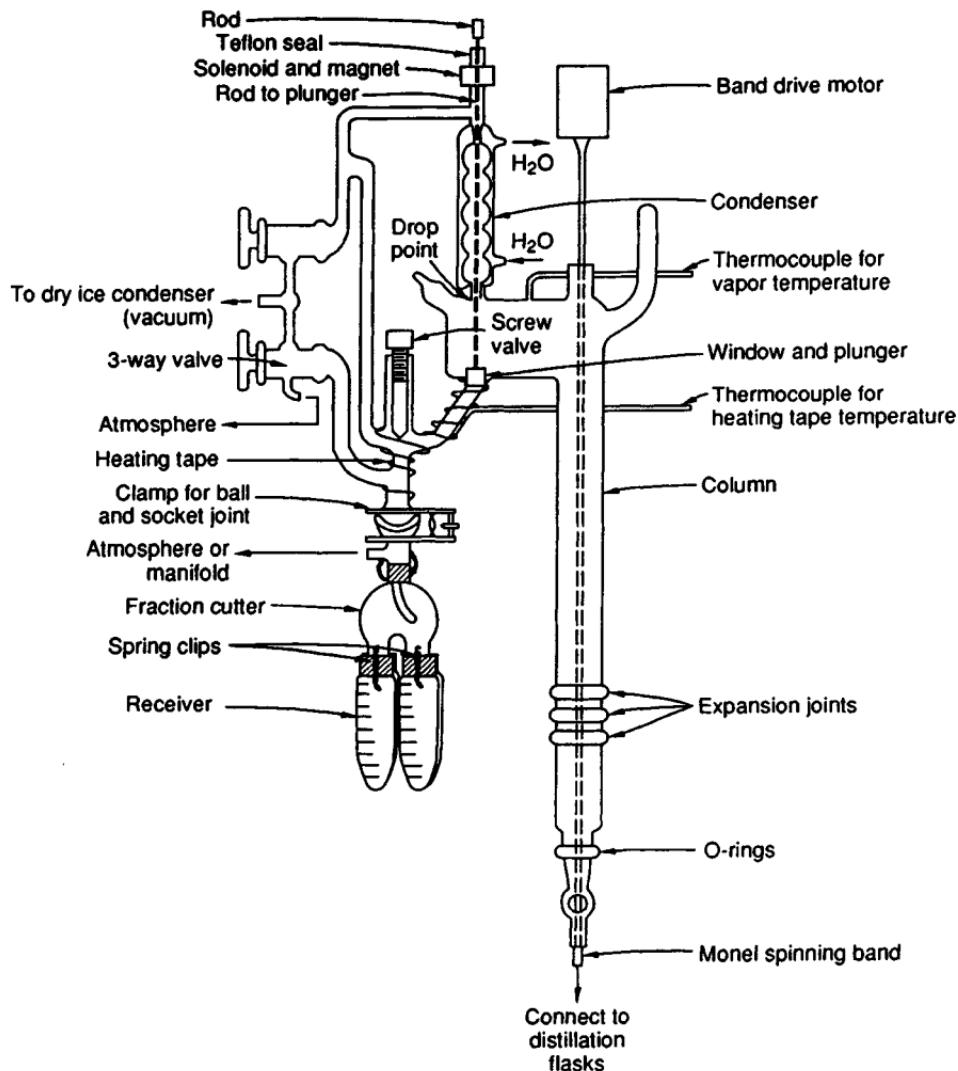


Figure 5.3. Schematic representation of the spinning band distillation apparatus (from Wallace, 1988).

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 using this equipment would be time consuming. In this 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 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.

Short path distillation permits collection of deeper-cut distillate and residue fractions than conventional vacuum distillation methods. AET end points of up to 660°C (1220°F) can be attained without thermal cracking of the material. The distillation, however, is conducted under nonequilibrium conditions so the cut point is not as specific as in other vacuum distillation methods.

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 used 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 (Tables 5.1 and 5.2) are considerably reproducible, particularly for the more volatile products.

One of the main properties of petroleum that serves to indicate the comparative ease with which the material can be refined is the volatility (Speight, 1999 and references cited therein). Investigation of the volatility of petroleum is usually

Table 5.1. Distillation Profile of Crude Oil (Leduc, Woodbend, Upper Devonian, Alberta, Canada) and Properties of the Fractions

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

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

Table 5.2. Distillation Profile of Bitumen (Athabasca, McMurray Formation, Upper Cretaceous, Alberta, Canada) and Properties of the Fractions

Feedstock Whole Bitumen Fraction*	Boiling Range		Wt% Cumulative	Specific Gravity 1.030	API Gravity 5.9	Sulfur Wt% 5.8	Carbon Residue (Conradson) 19.6
	°C	°F	Wt%	100.0			
1	0–50	0–122	0.0	0.0			
2	50–75	122–167	0.0	0.0			
3	75–100	167–212	0.0	0.0			
4	100–125	212–257	0.0	0.0			
5	125–150	257–302	0.9	0.9			
6	150–175	302–347	0.8	1.7	0.809	43.4	
7	175–200	347–392	1.1	2.8	0.823	40.4	
8	200–225	392–437	1.1	3.9	0.848	35.4	
9	225–250	437–482	4.1	8.0	0.866	31.8	
10	250–275	482–527	11.9	19.9	0.867	31.7	
11	<200	<392	1.6	21.5	0.878	29.7	
12	200–225	392–437	3.2	24.7	0.929	20.8	
13	225–250	437–482	6.1	30.8	0.947	17.9	
14	250–275	482–527	6.4	37.2	0.958	16.2	
15	275–300	527–572	10.6	47.8	0.972	14.1	
Residuum	>300	>572	49.5	97.3			39.6

*Distillation at 762 mmHg and then at 40 mmHg for fractions 11–15.

carried out under standard conditions, thereby allowing comparisons to be made between data obtained from various laboratories. One of the distillation (nondestructive) methods that has been standard, in addition to the ASTM methods, was developed by the US Bureau of Mines.

If a detailed fractionation of the sample is of secondary importance, it must be recognized that the general shape of a one-plate distillation curve is often adequate for making engineering calculations, correlating with other physical properties, and predicting the product slate (Nelson, 1958).

In the preliminary assay of crude oils, the method of distillation is often used in the United Kingdom (IP 24) to give a rough indication of the boiling range of crude oil. The test is very similar to the well-known method for gasoline distillation (ASTM D-86, IP 123) and is carried out at atmospheric pressure and under conditions of poor fractionation. With crude oils, the distillation is stopped at 300°C (570°F) to avoid excessive decomposition, and the distillate and residue can be further examined using tests such as specific gravity, sulfur content (ASTM D-129, IP 61), and viscosity (ASTM D445, IP 71). The tests give a rough indication of the quality of the products to be obtained from the crude and have been used to compare crude oils in respect to quality of the 300°C (570°F) cut point residuum. For example, the wax content or viscosity gives a pointer to the type of residual fuels obtainable from the crude oil.

Owing to the wide variation in the types of crude oil and to the fact that most companies have evolved their own assay methods, it has proved difficult to devise a rigid procedure to be followed in all cases, although there would be considerable advantages to be gained if this were possible. The procedure is, in essence, that followed by many companies.

The method is based on a true boiling point (TBP) 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 distillates, lubricants, residual fuel oil, and bitumen. A TBP distillation is one in which the test sample is physically distilled to produce fractions of the desired cut points.

The actual procedure involves the distillation of the crude oil in 1- to 5-gallon quantities in a column equivalent to 14 theoretical plates and with reflux adjusted to obtain a true boiling point versus yield relationship. Narrow fractions can be taken throughout the distillation, and the still pressure can be reduced as necessary to avoid decomposition in the higher boiling ranges. The fractionating distillation is continued to a relatively high temperature such as 370°C (700°F) equivalent temperature at 760 mm Hg absolute. The actual operating pressure of the still at this stage would be in the region of 2 mmHg absolute. The distillate fractions up to this point cover the light and middle distillates, and after the analysis of the required fractions in this range, curves relating the various properties to yield on fraction or on crude oil can be drawn. A series of residues can also be prepared by appropriate blending of distillates with the final residue, and after analysis, property relationships with yield can also be prepared for the residues.

From the TBP curve, the yields of products of a required boiling range can be deduced and fractions can be blended to match required products for further analysis or treatments. The residue (b.p. >370°C, >700°F) obtained from the TBP distillation quoted contains the main lubricating oil stock, and by further distillation under high vacuum a series of distillates can be prepared to cover the various lubricating oil grades. With a waxy crude oil, it is necessary to remove the wax from these distillates and further examine the wax-free lubricating oil distillates.

It is often useful in this type of crude oil assay to be able 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 (similar to the 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 (1110°F) (corrected to 760 mm Hg absolute) with many crude oils. Bearing in mind the limitations in accuracy of the temperature measurements in the high boiling ranges of crude it is possible to construct a wide-range boiling point curve for the crude by combining the results of the simple distillation with those of the main distillation. This method gives useful comparative and reproducible results that are often accurate enough for engineering purposes.

It is advantageous in any analytical, research, or development organization dealing with crude oil to collect information by the above methods on a standard series of distillates or residues from crude oils so that valuable comparisons become available as the data accumulate. These distillates should be prepared as near as possible to the boiling ranges that are known to be suitable for marketable products together with a true boiling point yield curve: The residuum ($>370^{\circ}\text{C}$, $>700^{\circ}\text{F}$) can be further fractionated, if required, using, however, a high vacuum still of sufficient capacity to give fractions in suitable quantity for subsequent analysis.

There is also another method that is increasing in popularity for application to a variety of feedstocks, and that is the method commonly known as *simulated distillation* (ASTM D-2887).

This is a low-resolution, temperature-programmed gas chromatographic analysis intended to simulate the time-consuming TBP distillation method. It is based on the observation that hydrocarbons generally are eluted from a nonpolar column in the order of their boiling point, with the retention time being converted to equivalent distillation temperatures. The accumulated detector response is related to the amount of sample distilled. In practice, the nonpolar stationary phases do discriminate to some extent among different classes of hydrocarbon. The retention time is a function of the adsorptive property of the stationary phase, the vapor pressure, and the heat of vaporization. The empirical correlation between the retention time and boiling point, usually established by running a series of *n*-alkanes, is not strictly valid for other hydrocarbon classes such as aromatic and cycloalkane derivatives, which show a tendency to elute earlier than *n*-alkanes having the same boiling points.

The method has been well researched in terms of development and application (Hickerson, 1975; Green, 1976; Stuckey, 1978; Vercier and Mouton, 1979; Thomas et al., 1983; Romanowski and Thomas, 1985; MacAllister and DeRuiter, 1985; Schwartz et al., 1987; Thomas et al., 1987). The benefits of the technique include good comparisons with other ASTM distillation data as well as application to higher boiling fractions of petroleum. In fact, data output includes the provision of the corresponding Engler profile (ASTM D-86) as well as the prediction of other properties such as vapor pressure and flash point (DeBruine and Ellison, 1973). When it is necessary to monitor product properties, as is often the case during refining operations, such data provide a valuable aid to process control and on-line product testing.

For a more detailed distillation analysis of feedstocks and products, a low-resolution, temperature-programmed gas chromatographic analysis has been developed to simulate the time-consuming TBP distillation. The method relies on the general observation that hydrocarbons are eluted from a nonpolar adsorbent in the order of their boiling points. The regularity of the elution order of the hydrocarbon components allows the retention times to be equated to distillation temperatures

(Green et al., 1964) and the term *simulated distillation by gas chromatography* (or *simdis*) is used throughout the industry to refer to this technique.

Simulated distillation by gas chromatography is often applied in the petroleum industry to obtain true boiling point data for distillates and crude oils (Butler, 1979). The principle involves gas chromatographic distillation (GCD) as a means of separating compounds by boiling point to produce a distillation profile.

In comparison to an actual distillation, simulated distillation by gas chromatography requires a very small sample (on the order of several microliters) to produce a full boiling range distribution profile for prediction of distillate yield and residue. In addition, simulated distillation by gas chromatography might take as little as 2 h, whereas a full distillation may take 2 days.

Simulated distillation for distillate fractions (ASTM D-2887) is designed predominantly for samples with a final boiling point below 538°C (1000°F) and is not suitable for the analysis of higher-boiling residua, heavy oil, or bitumen.

In gas chromatographic distillations, the nonpolar silicone gum stationary phase tends to bleed from the support in conventional packed columns at temperatures above 370–380°C (698–716°F). High-temperature gas chromatographic distillation offers the possibility of extending the range of the gas chromatographic distillation profile for heavy oil and bitumen.

Good agreement has been reported between the capillary and packed column methods for residua, heavy oil, and bitumen. The accuracy of the capillary method is determined by analyzing a mixture of 30% internal standard (a 300–350°C, 572–662°F petroleum fraction) with a measured amount (e.g., 70% by weight) of residuum. The boiling point distribution profile of the residuum, calculated from the profile for the mixture with the internal standard mathematically subtracted out, may deviate by less than 0.3% by weight at any temperature from the curve for the residuum alone.

The capillary method has been used to identify the cut point between a distillate and residuum produced by short-path distillation at an atmospheric boiling equivalent that could not have been identified using a conventional column.

The test method for the boiling range distribution of petroleum fractions by gas chromatography (ASTM D-2887) cannot be used to map the distillation profile of heavy oil and bitumen because it does not provide for the determination of the proportion of sample having a boiling point in excess of 538°C (>1000°F) residue in sample. The use of internal standards, and combinations of actual distillations and gas chromatographic distillation that provide a distillate fraction that can then be analyzed by gas chromatography, has already gained wide acceptance in the industry.

However, the method can be used as one of two standardized methods (ASTM D-2887, ASTM D-3710) 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 to 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 (Schwartz et al., 1987).

The *quality of distillation*, that is, *the degree of overlap between one fraction and the next*, is important in the evaluation of fractions from a crude. Typically, in a high-quality distillation, the contamination will be 2–4% of total crude at each cut temperature.

Flooding of the column and *cracking of the feedstock* are two serious problems during a true boiling point distillation. Flooding, which results from an excessive rate of heating, is the physical transport of liquid up the column and into the receiver. Cracking is thermal degradation of crude oil caused by high temperatures in the distillation pot, and it can occur at any temperature above 250°C (482°F), depending on the crude oil. It is indicated by the formation of a "fog" in the distillation pot or column, a sudden drop of vapor temperature at the top of the column, or the presence of light components in the heavy fractions as measured by gas chromatographic distillation.

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 mm Hg, the pressure measurement is too inaccurate and a discontinuity can arise in the 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.

5.3. LIQUEFACTION AND SOLIDIFICATION

The liquefaction and solidification of petroleum and various fractions seem to draw little attention in the standard petroleum science textbooks, and yet both properties are very important in the handling of petroleum and in refinery management. In fact, petroleum and the majority of petroleum products are liquids at ambient temperature, and problems that may arise from solidification during normal use are not common. Nevertheless, the *melting point* is a test (ASTM D-87, ASTM D-127, IP 55, IP 133) that is widely used by suppliers of wax and by wax consumers;

it is particularly applied to the highly paraffinic or crystalline waxes. Quantitative prediction of the melting point of pure hydrocarbons is difficult, but the melting point tends to increase qualitatively with the molecular weight and with symmetry of the molecule.

The *softening point* (ASTM D-36, ASTM D-2398, IP 58), defined as the temperature at which a disk of the material softens and sags downward a distance of 25 mm under the weight of a steel ball under strictly specified conditions, finds wider use for residua, asphalt, and bitumen. The *dropping point* (ASTM D-566, IP 132) is the near-equivalent test that is used for lubricating greases.

The *melting points* (cf. ASTM D-87, IP 55, melting point of paraffin wax; ASTM D-127, IP 133, melting point of petrolatum and microcrystalline wax) of the normal paraffins (Table 5.3) agree fairly well with the data for the lower crystalline paraffin waxes when the materials are compared on a molecular weight

Table 5.3. Melting Points of the *n*-Paraffins

Number of Carbon Atoms	Melting Point	
	°C	°F
1	-182	-296
2	-183	-297
3	-188	-306
4	-138	-216
5	-130	-202
6	-95	-139
7	-91	-132
8	-57	-71
9	-54	-65
10	-30	-22
11	-26	-15
12	-10	14
13	-5	23
14	6	43
15	10	50
16	18	64
17	22	72
18	28	82
19	32	90
20	36	97
30	66	151
40	82	180
50	92	198
60	99	210

basis, and this furnishes some of the best evidence for chemical constitution of macrocrystalline petroleum wax. The effect of symmetry is far greater than that of molecular weight and often offsets it. The branched-chain hydrocarbon usually melts far below the straight-chain compound of the same number of carbon atoms. The branched-chain hydrocarbon will often melt at a lower temperature than the normal paraffin equivalent to the longest chain in the molecule. Exceptions occur when the substitution produces a compact, symmetrical molecule, and similar qualitative rules apply to cyclic compounds.

Unsubstituted and symmetrically substituted compounds (e.g., benzene, cyclohexane, *p*-xylene, and naphthalene) melt at higher temperatures relative to the paraffin compounds of similar molecular weight; the unsymmetrical isomers generally melt at lower temperatures than the aliphatic hydrocarbons of the same molecular weight.

Unsaturation affects the melting point principally by its alteration of symmetry; thus ethane (-172°C , -278°F) and ethylene (-169.5°C , -273°F) differ only slightly, but the melting points of cyclohexane (6.2°C , 21°F) and cyclohexene (-104°C , -155°F) contrast strongly. All types of highly unsymmetrical hydrocarbons are difficult to crystallize; asymmetrically branched aliphatic hydrocarbons as low as octane and most substituted cyclic hydrocarbons comprise the greater part of the lubricating fractions of petroleum, crystallize slowly if at all, and on cooling merely take the form of glasslike solids.

Although the melting points of petroleum and petroleum products are of limited usefulness, except to estimate the purity or perhaps the composition of waxes, the reverse process, *solidification*, has received some, but again limited, attention in petroleum chemistry.

For example, the solidification point of paraffin wax (ASTM D-394) is an important monitor for the behavior and performance of wax. However, the test is somewhat limited in its application to heavy oil or bitumen because the complexity of these materials prevents careful and conscientious application of the test. Hence, more emphasis is placed on the reverse phenomena such as *melting point*, *dropping point*, *softening point*, and *pour point*. Indeed, the solidification of petroleum and petroleum products has been differentiated into four categories: *cloud point*, *pour point*, *freezing point*, and *congealing point*.

The *cloud point* of petroleum or a petroleum product is the temperature at which paraffin wax or other solidifiable compounds present in the oil appear as a haze when the sample is chilled under definitely prescribed conditions (ASTM D-2500, ASTM D-3117, IP 219, IP 444, IP 445, IP 446).

To determine the *cloud point* and the *pour point* (ASTM D-97, ASTM D-5327, ASTM D-5853, ASTM D-5949, ASTM D-5950, ASTM D-5985, IP 15, IP 219, IP 441) the oil is contained in a glass test tube fitted with a thermometer and immersed in one of three baths containing coolants. The sample is dehydrated and filtered at a temperature 25°C (45°F) higher than the anticipated cloud point. It

is then placed in a test tube and cooled progressively in coolants held at -1 to +2°C (30 to 35°F), -18 to -20°C (-4 to 0°F), and -32 to -35°C (-26 to -31°F), respectively. The sample is inspected for cloudiness at temperature intervals of 1°C (2°F). If conditions or oil properties are such that reduced temperatures are required to determine the pour point, alternate tests are available that accommodate the various types of samples.

Related to the cloud point, the wax appearance temperature or wax appearance point is also determined (ASTM D-3117, IP 389).

The *pour point* of petroleum or a petroleum product is determined using this same technique (ASTM D-97, IP 15), and it is the lowest temperature at which the oil pours or flows. It is actually 2°C (3°F) above the temperature at which the oil ceases to flow under these definitely prescribed conditions when it is chilled without disturbance at a standard rate. To determine the pour point, the sample is first heated to 46°C (115°F) and cooled in air to 32°C (90°F) before the tube is immersed in the same series of coolants as used for the determination of the cloud point. The sample is inspected at temperature intervals of 2°C (3°F) by withdrawal and holding horizontal for 5 s until no flow is observed during this time interval.

The pour point of a crude oil was originally applied to crude oil that had a high wax content. More recently, the pour point, like the viscosity, is determined principally for use in pumping and pipeline design calculations. Difficulty occurs in these determinations with waxy crude oils that begin to exhibit irregular flow behavior when wax begins to separate. These crude oils possess viscosity relationships that are difficult to predict in pipeline operations. In addition, some waxy crude oils are sensitive to heat treatment that can also affect their viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy crude oils. At the present time, long crude oil pipelines and the increasing production of waxy crude oils make an assessment of the pumpability of a wax-containing crude oil through a given system a matter of some difficulty that can often only be resolved after field trials. Consequently, considerable work is in progress to develop a suitable laboratory pumpability test (such as described in IP 230) that gives an estimate of minimum handling temperature and minimum line or storage temperature.

On the issue of wax in crude oil, crude oil having a high wax content presents difficulties in handling and pumping. Such crude oil produces distillate and residual fuels of high pour point and lubricating oils that are costly to dewax. Thus considerable study has been made of wax cracking or destruction processes.

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

More recently, the pour point has also found use as an indicator of the temperature at which crude oil or heavy oil will flow during in situ recovery operations (Wallace, 1988, p. 183). Under similar conditions, tar sand bitumen is immobile. For example, for asphaltic crude oils in which paraffin precipitation will not occur, if 21°C (70°F) is the pour point of a crude oil in a reservoir where the temperature is 38°C (100°F), the oil is liquid under reservoir conditions and will be mobile and will flow under those conditions. On the other hand, tar sand bitumen (pour point 60°C, 140°F) in a deposit (temperature 10°C, 50°F) will be solid and immobile. This state of the oil in the reservoir can also have consequences on the ability of gases and liquids (e.g., steam, hot water) used for recovery operations to penetrate the reservoir/deposit. Although pressure can have some influence on the pour point, the effect is not large and is unlikely to effect any general conclusions. Indeed, for specific types of petroleum (usually asphaltic and nonwaxy) there is a relationship between API gravity and pour point. Thus any increase in pour point due to an increase in pressure (surface compared to reservoir or deposit pressure) will be most likely be negated as the API gravity decreases with increase in temperature (60°F compared to reservoir temperature).

The solidification characteristics of a petroleum product depend on its grade or kind. For greases, the temperature of interest is that at which fluidity occurs, commonly known as the *dropping point*. The dropping point of grease is the temperature at which the grease passes from a plastic solid to a liquid state and begins to flow under the conditions of the test (ASTM D-566, ASTM D-2265, IP 132). For another type of plastic solid, including petrolatum and microcrystalline wax, both melting point and congealing point are of interest.

The *melting point* of a wax is the temperature at which the wax becomes sufficiently fluid to drop from the thermometer; the *congealing point* is the temperature at which melted petrolatum ceases to flow when allowed to cool under definitely prescribed conditions (ASTM D-938).

For another type of solid, paraffin wax, the solidification temperature is of interest. For such purposes, melting point is defined as the temperature at which the melted paraffin wax begins to solidify, as shown by the minimum rate of temperature change, when cooled under prescribed conditions. For pure or essentially pure hydrocarbons, the solidification temperature is the *freezing point*, the temperature at which a hydrocarbon passes from a liquid to a solid state (ASTM D-910, ASTM D-1015, ASTM D-1016, ASTM D-2386, IP 16, IP 434, IP 435).

The relationship of cloud point, pour point, melting point, and freezing point to one another varies widely from one petroleum product to another. Hence, their significance for different types of product also varies. In general, cloud, melting, and freezing points are of more limited value and each has a narrower range of application than the pour point. Cloud and pour points are useful for predicting the temperature at which the observed viscosity of an oil deviates from the true (Newtonian) viscosity in the low-temperature range. They are also useful for

identification of oils or when planning the storage of oil supplies, because low temperatures may cause handling difficulties with some oils.

5.4. CARBON RESIDUE

The carbon residue of crude oil and crude oil products is a measure of the propensity of the sample to form coke when combusted under specific conditions that require a limited supply of oxygen. The carbon residue of a petroleum sample might be considered to be analogous to the determination of fixed carbon for coal (ASTM D-3172, ASTM D-3173, ASTM D-3174, ASTM D-3175).

Petroleum products are mixtures of many compounds that differ widely in their physical and chemical properties. Some of them may be vaporized in the absence of air at atmospheric pressure without leaving an appreciable residue. Other nonvolatile compounds leave a *carbonaceous residue* when destructively distilled under such conditions. This residue is known as carbon residue when determined in accordance with prescribed procedures. Thus the term *carbon residue* is used here to denote the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product. The residue is not entirely composed of carbon but is a coke that can be changed further by heating.

The method was originally devised to determine the carbon-forming tendencies of diesel fuels and lubricating oils in internal combustion engines. Carbon residue values of various heavy feedstocks are indicative of the coke yields to be expected from these materials in refinery coking operations (Speight, 1999, 2000 and references cited therein).

There are two older methods for determining the carbon residue of a petroleum or petroleum product, the *Conradson method* (ASTM D-189, IP 13) and the *Ramsbottom method* (ASTM D-524, IP 14). Both are applicable to the relatively non-volatile portion of petroleum and petroleum products, which partially decompose when distilled at a pressure of 1 atmosphere. However, oils that contain ash-forming constituents have erroneously high carbon residues by either method unless the ash is first removed from the oil; the degree of error is proportional to the amount of ash.

The Conradson carbon method is the more usual test for determining the amount of carbon residue left after evaporation and pyrolysis (destructive distillation) of residua, heavy oil, and bitumen and is intended to provide some indication of relative coke-forming propensity. The amount of Conradson carbon residue is also corrected for the presence of mineral matter in the sample.

In this method (ASTM D-189), a weighed quantity of sample is placed in a crucible and subjected to destructive distillation. The equipment consists of a large porcelain crucible placed inside two iron crucibles and heated by a gas burner until all petroleum vapors are driven off. A known weight of oil (e.g., 10 g) is placed

inside the porcelain crucible, and the apparatus is assembled and heated at such a rate that the vapors start to burn within about 10 min. The flame is then adjusted so that they burn at the top of the chimney for a further 21–23 min. The crucibles are then heated to a cherry-red heat for a further 7–8 min, giving a total time of approximately 30 min.

The residue undergoes a cracking and coking reaction during severe heating for a fixed period of time. The crucible containing the carbonaceous residue is cooled in a desiccator and weighed. This residue is subsequently reduced to an ash by heating in a muffle furnace at 750°C (1380°F), allowed to cool, and weighed. The amount of residue is corrected for the ash content and reported as the Conradson carbon residue (CCR).

In the Ramsbottom carbon method (ASTM D-524) a known weight of the petroleum sample (proportional to the anticipated weight of residue) is heated in a hemispherical glass bulb of standard dimensions by a bath of molten solder at 550°C (1020°F) for 20 min. The carbon residue is weighed and recorded as % wt. Ramsbottom carbon.

Because of the extremely small values of carbon residue obtained by the Conradson and Ramsbottom methods when applied to the lighter distillate fuel oils, it is customary to distill such products to 10% residual oil and determine the carbon residue thereof. Such values may be used directly in comparing fuel oils, as long as it is kept in mind that the values are carbon residues on 10% residual oil and are not to be compared with straight carbon residues.

The mechanical design and operating conditions of such equipment have such a profound influence on carbon deposition during service that comparison of carbon residues between oils should be considered as giving only a rough approximation of relative deposit-forming tendencies. Recent work has focused on the carbon residue of the different fractions of crude oils, especially the asphaltenes (Speight, 1999). A more precise relationship between carbon residue and hydrogen content, H-to-C atomic ratio, nitrogen content, and sulfur content has been shown to exist (see also Nelson, 1974). These data can provide more precise information about the anticipated behavior of a variety of feedstocks in thermal processes (Roberts, 1989).

Although there is no exact correlation between the two methods it is possible to interconnect the data (ASTM D-189, ASTM D-524), but caution is advised when using that portion of the curve below 0.1% wt/wt CCR.

Recently, a newer method (Noel, 1984) has also been accepted (ASTM D-4530) that is very appealing to those situations in which only small amounts of the sample are available. The method only requires small amounts of sample and was originally developed as a *thermogravimetric method*. The carbon residue produced by this method is often referred to as the *microcarbon residue (MCR)*. Agreements between the data from the three methods are good, making it possible to interrelate all of the data from carbon residue tests (Long and Speight, 1989).

Like the Conradson carbon residue test and the Ramsbottom carbon residue test, the microcarbon residue method (ASTM D-4530, IP 398) also provides a measure of the relative coke-forming propensity of the sample under degradation conditions that simulate commercial coking operations. Ash-forming constituents and/or nonvolatile constituents present in the sample will add to the residue value determined. In the method, a weighed quantity of sample is placed into a glass vial and heated to 500°C (930°F) under a nitrogen atmosphere for a specific time, during which the sample undergoes cracking and coking. Nitrogen is used to remove the volatile materials. The carbonaceous residue is reported as *% microcarbon residue* of the original sample.

Even though the three methods have their relative merits, there is a tendency to advocate use of the more expedient microcarbon method to the exclusion of the detriment of the Conradson and Ramsbottom methods because of the lesser amounts required in the microcarbon method., which is somewhat less precise in practical technique.

There is a relationship between the carbon residue and the atomic H-to-C ratio, and this can be refined (Roberts, 1989) to a fairly universal linear correlation between the carbon residue (Conradson) and the H-to-C ratio:

$$\text{H/C} = 171 - 0.0115\text{CR(Conradson)}.$$

This equation holds within two limits; at H/C values = 1.71, where the carbon residue is zero (no coke formation) and H/C = 0.5, where the carbon residue is 100 (all the material converts to coke under test conditions). There is a relationship between the carbon residue (Conradson) and the nitrogen content.

The carbon residue (ASTM D-189, ASTM D-524, ASTM D-4530, IP 13, IP 14) is a property that can be correlated with several other properties of petroleum (Speight, 1999); hence it also presents indications of the volatility of the crude oil and the coke-forming (or gasoline-producing) propensity. However, tests for carbon residue are sometimes used to evaluate the carbonaceous depositing characteristics of fuels used in certain types of oil-burning equipment and internal combustion engines.

The fact that these correlations exist can best be explained in terms of the distribution of chemical species in these materials. In each, there are some molecules with a higher proportion of aromatic carbon and more heteroatoms that, because of these characteristics, have low H-to-C ratios and a high propensity for producing coke. The proportion of these coke precursors, of course, is higher in the higher-boiling fractions than in the lower-boiling fractions.

The application of the Conradson carbon residue determination to heavy feedstocks, such as Athabasca bitumen, requires that a correction be made for inorganic matter by determining the ash content of the carbon residue. In addition, the high

Conradson carbon residue of such feedstocks allows use of a smaller sample size together with correspondingly shorter burning and flame times.

5.5. ANILINE POINT

In the early days of petroleum refining, there was a need to determine the relative amounts of aromatic compounds and aliphatic compounds in various products. Thus the aniline point came into being and has been widely used in the past. The method still finds use, but it is somewhat limited to the popularity of yesteryear. However, it should not be completely discarded because of age!

The *aniline point* of petroleum or a petroleum product is actually the critical solution temperature of the two liquids (aniline and the sample), that is, the minimum temperature at which they are miscible in all proportions. The term is now most generally applied to the temperature at which exactly equal parts of the two are miscible. This value is more conveniently measured than the original value and is only a few tenths of a degree lower for most substances. Thus the aniline point is an approximate measure of the aromatic content of a mixture of hydrocarbons and is defined as the lowest temperature at which petroleum is completely miscible with an equal volume of aniline.

Although it is an arbitrary index, the aniline point (ASTM D-611, IP 2) has considerable value in the characterization of petroleum products. For oils of a given type it increases slightly with molecular weight; for those of given molecular weight it increases rapidly with increasing paraffinic character. As a consequence, it was one of the first properties proposed for the group analysis of petroleum products with respect to aromatic and naphthene content. It is used, alternately, even in one of the more recent methods. The simplicity of the determination makes it attractive for the rough estimation of aromatic content when that value is important for functional requirements, as in the case of the solvent power of naphtha and the combustion characteristics of gasoline and diesel fuel.

Because aromatics dissolve aniline more readily than paraffins or *iso*-paraffins, the lower the aniline point the higher the proportion of aromatics in the oil. Because, also, the higher the aromatic content of an oil, the lower the cetane number the aniline number can be used to indicate the probable behavior of a petroleum product in a diesel engine.

Determination of the aniline point requires that 5 ml of a carefully dried sample and aniline are placed in a test tube fitted with a thermometer and stirrer and enclosed in a larger tube to act as an air jacket. If, on stirring, the sample and aniline are completely miscible, the apparatus is cooled until the mixture is opaque. The temperature is then raised at $1^{\circ}\text{C}/\text{min}$ ($3^{\circ}\text{F}/\text{min}$) until the thermometer bulb is just visible. The temperature is then recorded as the aniline point. If, at atmospheric temperature, the oil and aniline are not completely miscible, the temperature is raised until

this occurs. The mixture is then cooled at 1°C/min (3°F/min) until the thermometer bulb is just obscured, when the temperature is recorded as the aniline point.

The aniline point is used in conjunction with the API gravity to determine the *diesel index*.

5.6. SPECIFIC HEAT

Specific heat is defined as the quantity of heat required to raise a unit mass of material through one degree of temperature (ASTM D-2766). Such a definition in fact describes specific heat capacity, and is not related to the heat capacity of water. The more common units of Btu/lb°F or cal/g°C (which are numerically equal, being effectively the ratio of the heat required to heat the substance to that required to heat water) are related to the SI unit by 1 Btu/lb°F = 1 cal/g°C = 4.1868 kJ/kg°K. In addition to the standard method for the determination of specific heat (ASTM D-2766), differential scanning calorimetry has also been used (ASTM E-1269).

The property is often required in estimating the amount of heat necessary to preheat a fuel oil or to preheat heavy oil in the reservoir before recovery. Knowledge of the specific heat of a fraction is of importance in determining net heat fluxes in all heating and cooling problems. Thus specific heats are extremely important engineering quantities in refinery practice because they are used in all calculations on heating and cooling petroleum products.

Many measurements have been made on various hydrocarbon materials, but the data for most purposes may be summarized by the general equation:

$$C = 1/d(0.388 + 0.00045t)$$

where C is the specific heat at t (°F) of an oil whose specific gravity 60/60°F is d ; thus, specific heat increases with temperature and decreases with specific gravity. For bitumen and heavy oil the equation has been modified. Thus:

$$C_p = [0.758 + 0.00339(t + 273)]/d^{0.5}$$

where C_p is the heat capacity (J/g °K, 1.0 = 0.24 Btu/lb °F), t is the temperature (°C), and d is the density (g/cm³). Another relationship (Bland and Davidson, 1967) is:

$$C_p = (0.6811 - 0.308d) + t(0.000815 - 0.000306d) \times (0.055K + 0.35)$$

where C_p is the heat capacity (J/g °K, 1.0 = 0.24 Btu/lb °F), t is the temperature (°F), K is the Watson characterization factor (Chapter 3), and d is the specific gravity (60°F/60°F).

On the other hand, after extensive testing of bitumen samples from the Athabasca deposit (Smith-Magowan et al., 1982), the following temperature-dependent equation was derived for the specific heat of bitumen covering the range 50°C to 300°C (122°F to 572°F):

$$C_p = 1.55745.219 \times 10^3 t - 8.686 \times 10^{-6} t^2$$

where C_p is the specific heat (heat capacity; J/g °K, 1.0 = 0.24 Btu/lb °F) and t is the temperature (°C). For most hydrocarbons, specific heat is almost a linear function of temperature (increasing as temperature increases). It decreases, however, as the density increases.

For liquids, specific heat normally implies measurements at constant (atmospheric) pressure. The value is not very dependent on pressure, and the value given is almost identical with the value obtained at constant volume. For gases, however, the values at constant pressure and constant volume are quite different, the value at constant pressure being the greater by an amount equal to the specific gas constant.

5.7. LATENT HEAT

There are two properties that represent phase transformations: the latent heat of fusion and the latent heat of vaporization. The latent heat of fusion, defined as the quantity of heat necessary to change a unit weight of solid to a liquid without any temperature change, has received only intermittent attention but, nevertheless, some general rules have been formulated.

Phase transformations (melting and vaporization or the reverse processes, etc.) are not accompanied by a sensible heat change (rise in temperature), although they are associated with heat absorption or evolution, and these heat effects are called latent heats. Such changes are normally measured at constant pressure and are thus enthalpy changes, although values for the constant volume (internal energy) changes are obtainable in thermodynamic tables. The unit is Btu/lb (1 Btu/lb = 2.326 kJ/kg).

Heat of vaporization is perhaps the most important latent heat in petroleum engineering. It decreases as the temperature rises and becomes zero at the critical temperature (this phenomenon forming, in fact, a useful indication of the critical point). The importance of latent heat has led to many methods of obtaining such data from temperature and the more readily obtainable physical properties such as density. These correlations, although they contain a degree of empiricism, are generally based on the Clausius-Clapeyron equation.

As with specific heat, values of latent heat are needed to calculate heat effects, particularly for distillation equipment.

Table 5.4. Latent Heat of Fusion of *n*-Paraffins

Formula	MP (°C)	Latent Heat of Fusion (cal/g)	Formula	MP (°C)	Latent Heat of Fusion (cal/g)
CH ₄	-182.6	14.5	C ₁₉ H ₄₀	32.0	51.6
C ₂ H ₆	-172.0	19.2	C ₂₀ H ₄₂	37.0	52.1
C ₃ H ₈	-189.9	16.2	C ₂₁ H ₄₄	40.5	52.5
C ₄ H ₁₀	-135.0	26.9	C ₂₂ H ₄₆	44.5	53.0
C ₅ H ₁₂	-131.5	27.4	C ₂₃ H ₄₈	47.5	52.9
C ₆ H ₁₄	-94.5	34.1	C ₂₄ H ₅₀	50.5	53.0
C ₇ H ₁₆	-91.0	34.4	C ₂₅ H ₅₂	54.0	53.3
C ₈ H ₁₈	-56.5	40.3	C ₂₆ H ₅₄	56.5	53.5
C ₉ H ₂₀	-51.0	41.0	C ₂₇ H ₅₆	59.5	53.7
C ₁₀ H ₂₂	-32.0	44.1	C ₂₈ H ₅₈	61.5	53.6
C ₁₁ H ₂₄	-26.5	44.6	C ₂₉ H ₆₀	63.5	53.6
C ₁₂ H ₂₆	-12.0	46.8	C ₃₀ H ₆₂	66.0	53.8
C ₁₃ H ₂₅	-6.5	47.4	C ₃₁ H ₆₄	68.0	54.0
C ₁₄ H ₃₀	+5.5	49.0	C ₃₂ H ₆₆	69.5	54.0
C ₁₅ H ₃₂	10.0	49.4	C ₃₃ H ₆₈	71.0	54.1
C ₁₆ H ₃₄	20.0	50.8			
C ₁₇ H ₃₆	22.5	50.8			
C ₁₈ H ₃₈	28.0	51.2			

For hydrocarbons, latent heats of fusion commerce at approximately 15 cal/g for methane, rising to 40 cal/g for octane, then gradually approaching a limiting value of 55 cal/g (Table 5.4). Branched paraffins usually have a lower latent heat of fusion than the normal isomers (Table 5.5); paraffin wax has a latent heat of fusion in the range of 50–60 cal/g.

The *latent heat of vaporization*, defined as the amount of heat required to vaporize a unit weight of a liquid at its atmospheric boiling point, is perhaps the most important property of the two and has received considerably more attention because of its connection with equipment design. The latent heat of vaporization at the atmospheric boiling point generally increases with increasing molecular weight (Table 5.6) and, for the normal paraffins, generally decreases with increasing temperature and pressure.

The latent heat of vaporization at any temperature can be described in terms of the latent heat at the normal boiling point:

$$L = \gamma L_B / (T / T_B)$$

where L is the latent heat of vaporization at the absolute temperature T , γ is a

Table 5.5. Latent Heat of Fusion of Various Hydrocarbons

Formula	Name	MP (°C)	Heat of Fusion	
			cal/g	cal/mol
<i>Branched Paraffins</i>				
C ₅ H ₁₂	2-Methylbutane	-160.5	16.9	1220
C ₇ H ₁₆	2-Methylhexane	-119.1	21.2	2120
C ₇ H ₁₆	3-Ethylpentane	-118.8	22.6	2260
C ₇ H ₁₆	2,2-Dimethylpentane	-125.0	14.0	1400
C ₇ H ₁₆	2,4-Dimethylpentane	-120.6	16.0	1600
C ₇ H ₁₆	3,3-Dimethylpentane	-134.5	16.9	1690
C ₇ H ₁₆	2,2,3-Trimethylbutane	-25.4	5.3	530
C ₈ H ₁₈	2,2,4-Trimethylpentane	-107.8	18.9	2160
C ₈ H ₁₈	Hexamethylethane	+104.0	14.9	1700
<i>Aliphatic Olefins</i>				
C ₂ H ₄	Ethylene	-169.5	25.0	700
C ₃ H ₆	Propylene	-184.9	16.7	700
C ₅ H ₁₀	Trimethylene	-134.2	25.7	1800
C ₈ H ₁₆	Diisobutylene	-101.0	16.8	1880
<i>Aromatic Hydrocarbons</i>				
C ₆ H ₆	Benzene	+5.5	30.1	2350
C ₇ H ₈	Toluene	-95.1	17.2	1580
C ₈ H ₁₀	<i>o</i> -Xylene	-25.3	29.3	3110
C ₈ H ₁₀	<i>m</i> -Xylene	-53.5	25.8	2740
C ₈ H ₁₀	<i>p</i> -Xylene	-13.2	38.1	4040
C ₈ H ₁₀	Ethylbenzene	-95.1	20.6	2180
C ₉ H ₁₂	Pseudocumene	-44.5	25.2	3030
C ₁₀ H ₈	Naphthalene	+80.0	36.0	4610
C ₁₀ H ₁₂	Camphene	+51.0	57.0	7600
C ₁₀ H ₁₄	Durene	+79.3	37.4	5020
C ₁₀ H ₁₄	Isodurene	-24.0	23.0	3080
C ₁₀ H ₁₄	Prehnitene	-7.7	20.0	2680
C ₁₀ H ₁₄	<i>p</i> -Cymene	-68.9	17.2	2310
C ₁₀ H ₁₄	<i>n</i> -Butylbenzene	-88.5	19.5	2620
C ₁₀ H ₁₄	<i>tert</i> -Butylbenzene	-58.1	14.9	2000
C ₁₀ H ₁₀	β -Methylnaphthalene	+34.1	20.1	2850
C ₁₂ H ₁₀	Diphenyl	+68.6	28.8	4440
C ₁₂ H ₁₈	Hexamethylbenzene	+165.5	30.4	4930
C ₁₃ H ₁₂	Diphenylmethane	+25.2	26.4	4440
C ₁₄ H ₁₀	Anthracene	+216.5	38.7	6890

(Continued)

Table 5.5. (Continued)

Formula	Name	MP (°C)	Heat of Fusion	
			cal/g	cal/mol
<i>Aromatic Hydrocarbons</i>				
C ₁₄ H ₁₀	Phenanthrene	+96.3	25.0	4450
C ₁₄ H ₁₀	Tolane	+60.0	28.7	5110
C ₁₄ H ₁₂	Stilbene	+124.0	40.0	7200
C ₁₄ H ₁₄	Dibenzil	+51.4	30.7	5600
C ₁₉ H ₁₆	Triphenylmethane	+92.1	21.1	5150
<i>Hydroaromatic Hydrocarbons and Naphthenes</i>				
C ₆ H ₁₀	Cyclohexene	-104.1	9.6	790
C ₆ H ₁₂	Cyclohexane	+6.2	7.4	620
C ₆ H ₁₂	Methylcyclopentane	-143.0	19.5	1640
C ₇ H ₁₄	1,2-Dimethylcyclopentane	-119.0	15.7	1540
C ₇ H ₁₄	Methylcyclohexane	-126.9	16.2	1590
C ₁₀ H ₁₀	Δ ₂ -Dihydronaphthalene	+23.9	22.4	2920
C ₁₄ H ₁₂	Dihydrophenanthrene	+94.0	17.6	3160

temperature correction factor obtained from graphical data (Nelson, 1958, p. 174), and L_B is the heat of vaporization at absolute normal boiling point T_B .

The latent heat decreases with temperature until it has a value of zero at the critical temperature. Furthermore, the critical temperature of a high-API gravity crude oil is lower than the critical temperature of a low-API gravity crude oil. Hence the latent heat curves of various crude oil will exhibit crossover points.

Table 5.6. Latent Heat of Vaporization of *n*-Paraffins at the Atmospheric Equivalent Boiling Point

Compound	Boiling Point		$H_{\text{vaporization}}$	
	°C	°F	Btu/lb	kcal/mol
Methane	-161	-258	219.2	1.96
Propane	-42	-44	183.1	4.49
Heptane	98	208	135.9	7.58
Decane	174	340	118.7	9.39
Tetradecane	253	487	103.4	11.4
Eicosane	343	649	87.8	13.8

5.8. ENTHALPY OR HEAT CONTENT

Enthalpy is the heat energy necessary to bring a system from a reference state to a given state.

Thus enthalpy is a measure of the amount of heat in a quantity of material relative to a suitable base temperature. It is normally measured at constant pressure and may thus be referred to as enthalpy. It is the sum of the total latent heat changes and the product of specific heats and temperatures for the system. The unit used is the same as that for latent heat (page 152) and its uses are in the preparation of heat balances.

Enthalpy is a function only of the end states and is the integral of the specific heats with respect to temperature between the limit states plus any latent heats of transition that occur within the interval. The usual reference temperature is 0°C (32°F). Enthalpy data are easily obtained from specific heat data by graphic integration or, if the empirical equation given for specific heat is sufficiently accurate, from the equation:

$$H = 1/d(0.388 + 0.000225t^2 - 12.65)$$

Generally, only differences in enthalpy are required in engineering design, that is, the quantity of heat necessary to heat (or cool) a unit amount of material from one temperature to another. Such calculations are very simple because the quantities are arithmetically additive, and the enthalpy for such a change of state is merely the difference between the enthalpies of the end states.

5.9. THERMAL CONDUCTIVITY

It is often necessary in refining as well as in the application of petroleum products to establish the optimum conditions for the transfer of heat as well as the cooling function of these materials. Thus a knowledge of the specific heat (page 151) is of considerable value in estimating the likely rise in temperature for a given set of heat transfer conditions. In many heat transfer problems, the viscosity may have a decided influence over the establishment of convection currents or volume flow if forced circulation is involved. Thus the thermal conductivity of the oil becomes a significant factor.

The thermal conductivity K of hydrocarbon oils (in cgs units) is given by the equation:

$$K = 0.28/d(l - 0.00054) \times 10^{-3}$$

where d is the specific gravity. The units of thermal conductivity have been

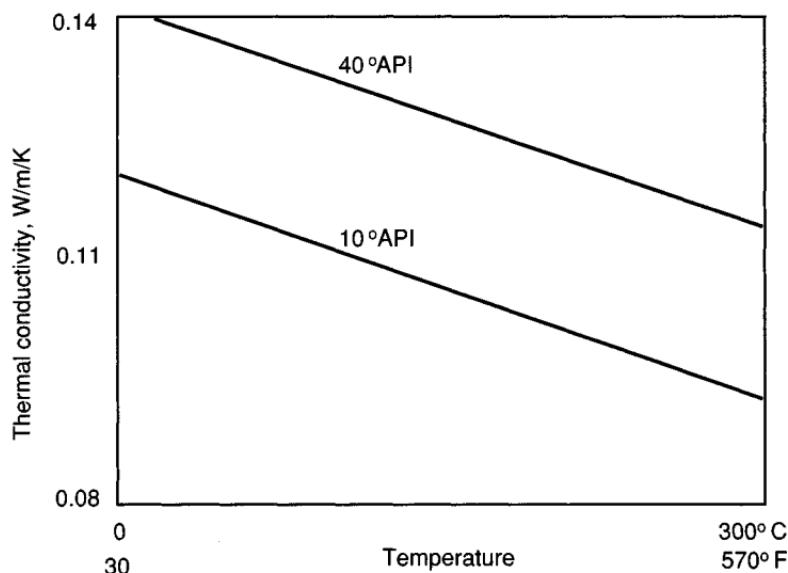


Figure 5.4. Thermal conductivity of petroleum liquids.

expressed as W/mK ($1.0 \text{ W/mK} = 0.86 \text{ kcal/h m } ^\circ\text{C} = 0.58 \text{ Btu/h ft } ^\circ\text{F}$). The thermal conductivity of a series of feedstocks can be estimated from the API gravity (Fig. 5.4) that shows a variation with temperature. The API gravity of bitumen and heavy oil varies from 6 to about 20. Thus at reservoir and deposit temperatures 0°C to 70°C (32°C 158°F), the value of bitumen thermal conductivity would thus be approximately 0.11 to about 0.12 (Fig. 5.4).

5.10. PRESSURE-VOLUME-TEMPERATURE RELATIONSHIPS

Knowledge of the pressure, volume, and temperature of a system forms the basis of the calculation of the thermodynamic relationships of the system. These properties are easily measured, and because they are sufficient to define the thermodynamic state they are termed the parameters of state. However, they are not independent, and, in fact, any two are sufficient to define the state of a system of known mass. A simple treatment of a mathematical model of a gas based on kinetic theory yields a relationship $PV = nRT$, where n is the number of moles of gas and R is a universal constant equal to $8.314 \text{ kJ/kmol}^\circ\text{K}$. This mathematical model is called the perfect gas, and real gases that behave in this way are called ideal gases. Most light petroleum gases, air, flue gases, etc. may be treated as ideal up to pressures of about $1.5\text{--}2 \text{ MN/m}^2$ (approximately $250\text{--}300 \text{ psi}$) provided the temperature is well

above the critical. For heavier vapors and for lower temperatures a more accurate equation of state is needed.

Sufficient accuracy is normally obtained for engineering purposes by the use of the compressibility coefficient (Z), where $PV = ZnRT$. The compressibility coefficient is a function of temperature, pressure, and the nature of the gas, but values can be obtained from generalized charts by use of reduced temperatures and pressures (pseudo-values in the case of mixtures).

In the calculation of pressure-volume-temperature relationships, it is often useful to use the concept of *standard conditions* at 0°C (32°F) and 1 atmosphere pressure (approximately 10^5 N/m^2); 1 kmol of the perfect gas occupies 22.4 m^3 [the corresponding value in British units is 359 ft a at 359 ft 3 and 1 atmosphere pressure or 379 ft 3 at 60°F and 1 atmosphere pressure (both values for 1 lb mole)]. When using these relationships it is important that both pressure and temperature be expressed in absolute scales. Gauge pressures and or $^\circ\text{C}$ or $^\circ\text{F}$ must not be used.

Hydrocarbon vapors, like other gases, follow the ideal gas law (i.e., $4PV = RT$) only at relatively low pressures and high temperatures, that is, far from the critical state. Several more empirical equations have been proposed to represent the gas laws more accurately, such as the well-known van der Waals equation, but they are either inconvenient for calculation or require the experimental determination of several constants. A more useful device is to use the simple gas law and to induce a correction, termed the *compressibility factor*, so that the equation takes the form:

$$PV = \mu RT$$

For hydrocarbons, the compressibility factor is very nearly a function only of the reduced variables of state, i.e., a function of the pressure and temperature divided by the respective critical values. The compressibility factor method functions excellently for pure compounds but may become ambiguous for mixtures because the critical constants have a slightly different significance. However, the use of pseudo-critical temperature and pressure values that are generally lower than the true values permits the compressibility factor to be employed in such cases.

5.11. HEAT OF COMBUSTION

The heat of combustion (ASTM D-240, IP 12) is a direct measure of fuel energy content and is determined as the quantity of heat liberated by the combustion of a quantity of fuel with oxygen in a standard bomb calorimeter.

Chemically, it is the energy (heat) released when an organic compound is burned to produce water ($\text{H}_2\text{O}_{\text{liquid}}$) carbon dioxide ($\text{CO}_{2\text{gas}}$), sulfuric acid ($\text{H}_2\text{SO}_{4\text{liquid}}$), and nitric acid ($\text{HNO}_{3\text{liquid}}$). The value can be calculated using a theoretical

equation based upon the elemental composition of the feedstock:

$$H_g/4.187 = 8400C + 27,765H + 1500N + 2500S - 2650O$$

where H_g is given in kilojoules per kilogram (1.0 kJ/kg = 0.43 Btu/lb), C, H, N, S, and O are the normalized weight fractions for these elements in the sample.

The gross heats of combustion of crude oil and its products are also given with reasonable accuracy by the equation:

$$Q = 12,400 - 2100d^2$$

where d is the 60/60°F specific gravity. Deviation is generally less than 1%, although many highly aromatic crude oils show considerably higher values; the range for crude oil is 10,000 to 11,600 cal/g (Speight, 1999, p. 341). For gasoline, the heat of combustion is 11,000 to 11,500 cal/g (1.0 cal/g = 1.80 Btu/lb) and for kerosene (and diesel fuel) it falls in the range 10,500 to 11,200 cal/g. Finally, the heat of combustion for fuel oil is on the order of 9,500 to 11,200 cal/g. Heavy oil and bitumen have a heat of combustion of 9,800 to 10,200 cal/g (Table 5.7). Heats of combustion of petroleum gases may be calculated from the analysis and data for the pure compounds. Experimental values for gaseous fuels may be obtained by measurement in a water flow calorimeter, and heats of combustion of liquids are usually measured in a bomb calorimeter.

For thermodynamic calculation of equilibria useful in hydrocarbon research, combustion data of extreme accuracy are required because the heats of formation of water and carbon dioxide are large in comparison with those in the hydrocarbons. Great accuracy is also required of the specific heat data for the calculation of free energy or entropy. Much care must be exercised in selecting values from the

Table 5.7. Heats of Combustion of Alberta (Canada) Heavy Oil and Bitumen

Heavy Oil or Bitumen	Heat of Combustion		
	Btu/lb	cal/g	kJ/kg
<i>Athabasca</i>			
Mildred Lake	18,030	10,025	41,940
<i>Carbonate</i>			
Grosmont	17,570–17,650	9765–9810	40,865–41,050
<i>Cold Lake</i>			
Clearwater	17,975–18,300	9990–10,170	41,810–42,530
Lloydminster	17,975–18,285	9990–10,165	41,810–42,530
Peace River	17,750–18,020	9880–10,020	41,350–42,530
Wabasca	17,875–18,440	9935–10,230	41,580–42,800

literature for these purposes, because many of the available values were determined before the development of modern calorimetric techniques.

An alternative criterion of energy content is the aniline gravity product (AGP) (ASTM D-1405, IP 193), which is in reasonable agreement with the calorific value. It is the product of the API gravity and the aniline point (ASTM D-611, IP 2) of the sample.

The combustion characteristics of petroleum and petroleum products can also be evaluated by the application of several other tests.

Jet fuels of the same class can vary widely in burning quality as measured by carbon deposition, smoke formation, and flame radiation. This quality aspect is largely a function of hydrocarbon composition because paraffins have excellent burning properties in contrast to those of the aromatic compounds (particularly polynuclear aromatics); naphthenes have intermediate combustion characteristics nearer to those of the paraffins.

As a control measure the smoke point test (ASTM D-1322 or 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:

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

The smoke point test is not universally accepted as a completely reliable criterion of combustion performance, and various alternative laboratory test methods have previously been specified such as the lamp burning test (ASTM D187, IP 10) and a limit on the polynuclear aromatic content (ASTM D1840). However, the alternative test now generally accepted is the luminometer number (ASTM D1740). This test was developed to accommodate the shortened combustion chamber in many jet engines that is due to high liner temperatures caused by the radiant heat from luminous flames from certain qualities of fuel. The test apparatus is essentially a smoke point lamp modified to include a photoelectric cell for flame radiation measurement and a thermocouple arrangement 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 reference fuels tetralin and iso-octane, respectively.

5.12. CRITICAL PROPERTIES

A study of the pressure, volume, and temperature relationships of a pure component reveals a particular unique state at which the properties of a liquid and vapor become indistinguishable from each other. At that state, the latent heat of vaporization becomes zero and no volume change occurs when the liquid is vaporized. This

state is called the critical state, and the appropriate parameters of state are termed the critical pressure (P_C), critical volume (V_C), and critical temperature (T_C). It is an important characteristic of the critical state for a pure component that with values of P or T greater than either P_C or T_C the vapor and liquid states cannot coexist at equilibrium, and thus P_C and T_C represent the maximum values of P and T at which phase separation can occur.

Because the critical state of a component is unique, it is perhaps not surprising that knowledge of P_C , T_C , and V_C allows many predictions to be made concerning the physical properties of substances. These predictions are based on the law of corresponding states, which states that substances behave in the same way when they are in the same state with reference to the critical state. The particular corresponding state is characterized by its reduced properties, i.e., $T_r = T/T_C$, $P_r = P/P_C$, $V_r = V/V_C$.

The use of this concept permits generalized plots in terms of reduced properties to be drawn that are then applicable to all substances (which obey the law) and can be of great value in determining thermodynamic relationships. It is rare in petroleum engineering to have to deal with pure substances, and unfortunately the application of the law of corresponding states to mixtures is complicated by the fact that use of the true critical point for a mixture does not yield correct values of reduced properties for accurate prediction from generalized charts. For a mixture, the critical state no longer represents the maximum temperature and pressure at which a liquid and vapor phase can coexist, and phase separation can occur under retrograde conditions.

For engineering purposes, this difficulty is resolved by the use of pseudo-critical conditions, which are based on the molal average critical temperatures and pressures of the compounds of the mixture. Although use of pseudo-reduced conditions for mixtures of hydrocarbons is generally satisfactory, this is not true for states near the true critical, nor, in general, for mixtures of vapor and liquid.

The temperature, pressure, and volume at the critical state are of considerable interest in petroleum physics, particularly in connection with modern high-pressure, high-temperature refinery operations and in correlating pressure-temperature-volume relationships for other states. Critical data are known for most of the lower-molecular-weight pure hydrocarbons, and standard methods are generally used for such determinations.

The *critical point* of a pure compound is the equilibrium state in which its gaseous and liquid phases are indistinguishable and coexistent; they have the same intensive properties. However, localized variations in these phase properties may be evident experimentally. The definition of the critical point of a mixture is the same. However, mixtures generally have a maximum temperature or pressure at other than the true critical point; *maximum* here denotes the greatest value at which two phases can coexist in equilibrium.

Thus, when a pure compound is heated at atmospheric pressure, it eventually reaches its boiling point and is completely vaporized at a constant temperature

unless the pressure is increased. If the pressure is increased, the compound is completely condensed and cannot be vaporized again unless the temperature is also increased. This mechanism, alternately increasing the pressure and temperature, functions until, at some high temperature and pressure, it is found that the material cannot be condensed regardless of the amount of pressure applied. This point is called the *critical point*, and the temperature and pressure at the critical point are called the *critical temperature* and *critical pressure*, respectively.

The liquid phase and vapor phase merge at the critical point so that one phase cannot be distinguished from the other. No volume change occurs when a liquid is vaporized at the critical point and no heat is required for vaporization, but the coefficient of expansion has become large.

Limited information concerning the behavior of complex mixtures has required that the pseudo-critical temperature and pseudo-critical pressure be used for many petroleum fractions and products. The *pseudo-critical point* is defined as the molal average critical temperature and pressure of the several constituents that make up a mixture. It may be used as the critical point of a mixture in computing reduced temperatures and pressures. However, in computing the pressure-volume-temperature relations of mixtures by use of the pseudo critical point, it must be recognized that the values are not accurate in the region of the critical point-and that it cannot be applied to mixtures of gas and liquid.

In the correlation of many properties, reduced properties are useful. *Reduced properties* are defined as the ratio of the actual value of the property to its critical value. Thus for volume, temperature, or pressure the relationships are:

$$\text{reduced volume, } V_R = V/V_c$$

where V is the volume at specified conditions and V_c is the volume at the critical point. Similarly,

$$\text{reduced temperature } T_R = T/T_c$$

and

$$\text{reduced pressure } P_R = P/P_c$$

Where T and V are the temperature and volume, respectively, at specified conditions and T_c and V_c are the temperature and volume, respectively, at the critical point.

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CHAPTER

6

ELECTRICAL AND OPTICAL PROPERTIES

6.1. INTRODUCTION

By way of introduction and to restate the concept of earlier chapters, petroleum is a complex mixture of chemical compounds and exhibits a wide range of physical properties. The *standard* properties such as viscosity, density, boiling point, and color of petroleum were the benchmark by which petroleum was identified.

However, as the complexities of refineries increased to meet the demands of changing feedstocks and included the heavier feedstocks such as heavy oil and bitumen, the nature and range of the tests carried out to aid in developing behavior profiles for the feedstocks also became more complex. And although the chemical composition of a feedstock is a much truer indicator of refining behavior (Nelson, 1958; Gruse and Stevens, 1960; Gary and Handwerk, 1984; Ali et al., 1985; Wallace et al., 1988; Speight, 2000), it is often not applicable to all of the operations that are a different reflection of feedstock behavior in a refinery. Therefore, the judicious choice of test methods for any refinery feedstock are just as important as the selection of the feedstock to produce a specific slate of products.

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

Thus, the inspection or evaluation methods must give as much information as possible about the complete character of the crude oil to provide information about the most logical means of feedstock handling before and during refining. Indeed, careful evaluation of petroleum from physical property data must be a major part of the study of any crude oil, heavy oil, or bitumen that is destined to be a refinery feedstock. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of their significance.

In this chapter an indication of the additional physical properties not covered elsewhere (Chapters 4 and 5) that may be applied to petroleum, or even to petroleum products, is presented. The properties covered here are properties that are not often given the attention they deserve.

Although the physical properties of petroleum and petroleum products are often equated with those of the various related hydrocarbons, the electrical and optical properties of pure hydrocarbons have been investigated to a lesser degree than the so-called *typical physical properties*, leaving considerable gaps in knowledge. Thus very little is known about the electrical and optical properties of crude oil.

For the purposes of this chapter, data relating to various physical properties are included as illustrative examples where possible but theoretical discussions of the physical properties of hydrocarbons were deemed irrelevant and are omitted.

6.2. ELECTRICAL PROPERTIES

The electrical properties of crude oil and crude oil products (especially lubricating oils) can be of considerable practical significance. The development of electrostatic charges in pipelines, in refinery equipment, and in machinery is well known. When electrical discharges occur through an oil film, observable changes in metal surfaces can be expected and are usually reflected in the occurrence of pitting. On the other hand, changes in the crude oil (or its products) might result in sediment or gum formation, causing problems in refining and product use.

This area of petroleum technology has not been researched as thoroughly as the other *more conventional* areas. Thus the electrical properties of petroleum and its products represent a fertile area of investigation for the analytical chemist as a result of a definite need to establish tests that are representative of the behavior of crude oil under these conditions.

6.2.1. Electrical Conductivity

From the fragmentary evidence available, the electrical conductivity of hydrocarbons is quite small. For example, the normal hydrocarbons (from hexane up) have an electrical conductivity smaller than $10^{-16} \Omega/\text{cm}$; benzene itself has an electrical conductivity of $4.4 \times 10^{-17} \Omega/\text{cm}$, and cyclohexane has an electrical conductivity of $7 \times 10^{-18} \Omega/\text{cm}$. It is generally recognized that hydrocarbons do not usually have an electrical conductivity larger than $10^{-18} \Omega/\text{cm}$. Thus it is not surprising that the electrical conductivity of crude oils or crude oil fractions (ASTM D-3114, IP 274) that are predominantly hydrocarbon in nature is also exceedingly small, of the order of $10^{-19}\text{--}10^{-12} \Omega/\text{cm}$.

Available data indicate that the observed conductivity is frequently more dependent on the method of measurement and the presence of trace impurities than

on the chemical type of the oil. Conduction through oils is not ohmic; that is, the current is not proportional to field strength. In some regions the current is observed to increase exponentially with the field strength. Time effects are also observed, the current being at first relatively large and decreasing to a smaller steady value. This is partly because of electrode polarization and partly because of ions removed from the solution. Most oils increase in conductivity with rising temperatures.

6.2.2. Dielectric Constant

The *dielectric constant* (ϵ) of a substance may be defined as the ratio of the capacity of a condenser with the material between the condenser plates (C) to that with the condenser empty and under vacuum (C_0):

$$\epsilon = C/C_0$$

The dielectric constant of petroleum and petroleum products is also theoretically equal to the square of the refractive index.

The dielectric constant (ASTM D-924) may be used to indicate the presence of various constituents, such as asphaltenes, resins, or oxidized materials, i.e. materials that are polar in nature and more capable of conducting electricity. In these cases, the dielectric constant may be higher than that calculated using the square of the refractive index. Furthermore, the dielectric constant of petroleum products that are used in equipment, such as condensers, may actually affect the electrical properties and performance of that equipment (ASTM D-877).

The dielectric constant of hydrocarbons, and hence most crude oils and their products, is usually low and decreases with an increase in temperature (Table 6.1). It is also noteworthy that for hydrocarbon materials the dielectric constant is approximately equal to the square of the refractive index (Table 6.2). Polar materials have dielectric constants greater than the square of the refractive index (page 170).

6.2.3. Dielectric Strength

The dielectric strength, or breakdown voltage (ASTM D-877; see also IP 295), is the greatest potential gradient or potential that an insulator can withstand without permitting an electric discharge. The property is, in the case of oils as well as other dielectric materials, somewhat dependent on the method of measurement, that is, on the length of path through which the breakdown occurs, the composition, shape, and condition of the electrode surfaces, and the duration of the applied potential difference.

The standard test used in North America is applied to oils of petroleum origin for use in cables, transformers, oil circuit breakers, and similar apparatus. Oils of high purity and cleanliness show nearly the same value under standard conditions,

Table 6.1. Dielectric Constants of Hydrocarbons and Petroleum Products

Material	Temperature		Dielectric Constant
	°C	°F	
<i>n</i> -Hexane	0	32	1.918
	20	68	1.890
	60	140	1.817
<i>n</i> -Heptane	0	32	1.958
	20	68	1.930
	60	140	1.873
Benzene	10	50	2.296
	20	68	2.283
	60	140	2.204
Cyclohexane	20	68	2.055
Petroleum products			
Gasoline	20	68	1.8-2.0
Kerosene	20	68	2.0-2.2
Lubricating oil	20	68	2.1-2.6

generally ranging from 30 to 35 kV. For alkanes, dielectric strength has been shown to increase linearly with liquid density, and the value for a mineral oil fits the data well. For *n*-heptane, a correlation was found between the dielectric strength and the density changes with temperature. There are many reasons that the dielectric strength of an insulator may fail. The most important appears to be the presence of some type of impurity, produced by corrosion, oxidation, thermal or electrical cracking, or gaseous discharge; invasion by water is a common trouble.

Table 6.2. Relationship of the Refractive Index to the Dielectric Constant of Hydrocarbons and Petroleum Products

Material	Refractive Index <i>n</i>	<i>n</i> ²	Dielectric Constant
Benzene	1.501	2.253	2.283
Cyclohexane	1.427	2.036	2.055
<i>n</i> -Hexane	1.375	1.890	1.890
<i>n</i> -Heptane	1.388	1.926	1.933
Kerosene	1.449	2.100	2.135
Paraffin oil	1.481	2.193	2.195
Vaseline	1.480	2.190	2.078

6.2.4. Dielectric Loss and Power Factor

A condenser insulated with an ideal dielectric shows no dissipation of energy when an alternating potential is applied. The charging current, technically termed the *circulating current*, lags exactly 90° in phase angle behind the applied potential, and the energy stored in the condenser during each half-cycle is completely recovered in the next. No real dielectric material exhibits this ideal behavior; that is, some energy is dissipated under alternating stress and appears as heat. Such a lack of efficiency is broadly termed *dielectric loss*.

Ordinary conduction comprises one component of dielectric loss. Here the capacitance-held charge is partly lost by short circuit through the medium. Other effects in the presence of an alternating field occur, and a dielectric of zero conductivity may still exhibit losses. Suspended droplets of another phase undergo spheroidal oscillation by electrostatic induction effects and dissipate energy as heat as a consequence of the viscosity of the medium. Polar molecules oscillate as electrets and dissipate energy on collision with others. All such losses are of practical importance when insulation is used in connection with alternating-current equipment.

The measure of the dielectric loss is the power factor (ASTM D-877). This is defined as the factor k in the relation:

$$k = W/EI$$

where W is the power in watts dissipated by a circuit portion under voltage E and passing current I .

From ac theory, the power factor is recognized as the cosine of the phase angle between the voltage and current where a pure sine wave form exists for both; it increases with a rise in temperature. When an insulating material serves as the dielectric of a condenser, the power factor is an intrinsic property of the dielectric. For practical electrical equipment, low-power factors for the insulation are of course always undesirable; petroleum oils are generally excellent in this respect, having values of the order of 0.0005, comparable with fused quartz and polystyrene resins. The power factor of pure hydrocarbons is extremely small. Traces of polar impurities, however, cause a striking increase. All electrical oils, therefore, are drastically refined and handled with care to avoid contamination; insoluble oxidation products are particularly undesirable.

6.2.5. Static Electrification

Dielectric liquids, particularly light naphtha, may acquire high static charges on flowing through or being sprayed from metal pipes. The effect seems to be associated with colloidally dispersed contaminants, such as oxidation products, which

can be removed by drastic filtration or adsorption. Because a considerable fire hazard is involved, a method has evolved for obtaining data that will help to minimize the potential danger (ASTM D-4470).

For large-scale storage, avoidance of surface agitation and use of floating metal roofs on tanks are beneficial. High humidity in the surrounding atmosphere is helpful in lowering the static charge, and radioactive materials have been used to try to induce discharge to ground. A variety of additives have been found that increase the conductivity of petroleum liquids, thus lowering the degree of electrification; chromium salts of alkylated salicylic acids and other salts of alkylated sulfosuccinic acids are used in low concentrations, for example, 0.005%.

6.3. OPTICAL PROPERTIES

6.3.1. Color

The most obvious optical property of petroleum and petroleum products is the color of the material. In these days when heavy oils, residua, and bitumen are refinery feedstocks and these materials are generally black, the color test has lesser significance in the preliminary inspection of the feedstock.

However, the color tests continue to play an important role in determining the purity and/or the stability of petroleum products (Mushrush and Speight, 1995), for example, tests for the acid or basic nature of petroleum products by color titration (ASTM D-974, IP 139, 213, IP 431), the Doctor test for sulfur species (ASTM D-4952), the color of aviation gasoline (ASTM D-2392), the color of petroleum products using a color scale (ASTM D-1500, IP 17, IP 196), and the color of petroleum products using the Saybolt chromometer (ASTM D-156). In fact, the test for the color of petroleum products (ASTM D-1500) can, if desired, be adapted to heavy oil and bitumen by applying the test to specifically diluted solution of heavy oil or bitumen in a colorless solvent such as toluene.

6.3.2. Refractive Index

The *refractive index* (ASTM D-1218, ASTM D-1747) is the ratio of the velocity of light in a vacuum to the velocity of light in the substance. The refractive index can be used to give information about the composition of hydrocarbon mixtures (ASTM D-2140, ASTM E-1303, IP 346, IP 391, IP 436). As with density, (Chapter 4) low values are typical of paraffins and higher values are typical of aromatic compounds.

The measurement of the refractive index is very simple (ASTM D-1218). It requires small quantities of material and, consequently, has found wide use in the characterization of hydrocarbons and petroleum samples.

This method (ASTM D-1218) covers the measurement of the refractive index of liquid petroleum and petroleum products in the range of 1.3300–1.6500. Typically, the measurement is carried out at 20°C (68°F). Most instruments are capable of operation from 5°C to 40°C (41°F to 104°F).

In a critical angle refractometer, light is directed at the interface between a prism and the sample at a range of angles. At the critical angle, the light changes from penetrating the sample to being totally reflected back into the prism from the interface. Knowing the angle at which this happens and the properties of the prism, the refractive index (RI) may be determined. The specified unit measures this angle, applies appropriate corrections if required, and displays the refractive index directly on a digital display. The temperature of the prism may also be displayed. The advantage of the critical angle unit is that the light is not passed through the sample, as in the Abbé refractometer. This makes the critical angle unit suitable for highly colored liquids as well as clear liquids, in contrast to the Abbé refractometer, which cannot measure dark liquids.

A critical angle refractometer measures the very thin layer of liquid that contacts the prism, typically the continuous phase of the sample. It will frequently not be influenced by suspended or dispersed material in the sample. Emulsions and very fine dispersions may influence the unit. A particulate-free, single-phase sample is far better, but one containing these inclusions is not automatically excluded.

For closely separated fractions of similar molecular weight, the values increase in the order paraffin, naphthene, aromatic. For polycyclic naphthenes and polycyclic aromatics, the refractive index is usually higher than that of the corresponding monocyclic compounds. For a series of hydrocarbons of essentially the same type the refractive index increases with molecular weight, especially in the paraffin series (Table 6.3). Thus the refractive index can be used to provide valuable information about the composition of hydrocarbon (petroleum) mixtures; as with density, low values indicate paraffinic materials and higher values indicate the presence of aromatic compounds. However, the combination of refractive index and density may be used to provide even more definite information about the nature of a hydrocarbon mixture and, hence, the use of derived data such as the refractivity intercept ($n - d/2$) (Table 6.4) (ASTM D-2140, ASTM D-2159) and the specific refraction $[(n^2 - 1)/(n^2 + 2) \times 1/d]$ as being indicative of the composition of hydrocarbon mixtures.

The refractive index of viscous materials [including viscous liquids and melted solids have refractive indices between 1.33 and 1.60 and at temperatures from 80°C to 100°C (176°F to 212°F)]. However, the method is not applicable to liquids that have colors darker than ASTM Color No. 4 (ASTM D-1500) or to solids that melt within 10°C (18°F) of the test temperature. These caveats may disqualify many types of heavy oil (because of the color) and bitumen (because of the high

Table 6.3. Refractive Indices of Hydrocarbons

Hydrocarbon	$n_D^{20^a}$
Pentane	1.3579
Hexane	1.3749
Heptane	1.3876
Octane	1.3975
Nonane	1.4054
Decane	1.4119
Nonadecane	1.4409
Eicosane	1.4425
Cyclopentane	1.4064
Cyclohexane	1.4266
Cycloheptane	1.4449
Benzene	1.5011
Toluene	1.4961
Ethylbenzene	1.4959
Propylbenzene	1.4920
Tetralin	1.5461
Decalin	1.4811

^a n_D^{20} : Refractive index at 20°C (68°F) at the wavelength of the sodium D line.

melting point, ASTM D-87 and D-127, or the high pour point, ASTM D-97 (Chapter 5).

The *refractive dispersion* of a substance is defined as the difference between its refractive indices at two specified wavelengths of light (ASTM D-1218). Two lines commonly used to calculate dispersions are the C (6563 D, red) and F (4861 D, blue) lines of the hydrogen spectrum. The specific dispersion is the refractive

Table 6.4. Refractivity Intercept for Hydrocarbon Types

Paraffin	1.0461
Saturated monocyclics	1.0400
Saturated polycyclics	1.0285
Olefins	1.0521
Diolefins	1.0592
Conjugated diolefins	1.0877
Cycloolefins	1.0461
Conjugated cyclodiolefins	1.0643
Aromatics	1.0627

dispersion divided by the density at the same temperature:

$$\text{specific dispersion} = n_F - n_C/d$$

This equation is of particular significance in petroleum chemistry because all the saturated hydrocarbons, naphthene and paraffin, have nearly the same value irrespective of molecular weight, whereas aromatics are much higher and unsaturated aliphatic hydrocarbons are intermediate. The refractive and specific dispersion (ASTM D-1807) as well as the molecular and specific refraction have all been advocated for use in the characterization of petroleum and petroleum products.

Specific refraction is the term applied to the quantity defined by the expression:

$$n - 1/(n^2 + 2)d = C$$

where n is the refractive index, d is the density, and C is a constant independent of temperature.

Molecular refraction is the specific refraction multiplied by molecular weight; its particular usefulness lies in the fact that it is very nearly additive for the components of a molecule; that is, numerical values can be assigned to atoms and structural features, such as double bonds and rings. The value for any pure compound is then approximately the sum of such component constants for the molecule.

6.3.3. Optical Activity

The occurrence of optical activity in petroleum is universal and is a general phenomenon not restricted to a particular type of crude oil, such as the paraffinic or naphthenic crude oils. Petroleum is usually *dextrorotatory*, that is, the plane of polarized light is rotated to the right, but there are known *levorotatory* crude oils, that is, the plane of polarized light is rotated to the left, and some crude oils have been reported to be optically inactive.

Examination of the individual fractions of optically active crude oils shows that the rotatory power increases with molecular weight (or boiling point) to pronounced maxima and then decreases again. The rotatory power appears to be concentrated in certain fractions, the maximum lying at a molecular weight of about 350–400; this maximum is about the same for all crude oils. The occurrence of optically active compounds in unaltered natural petroleum has been a strong argument in favor of a rather low temperature origin of petroleum from organic raw materials (Speight, 1999).

A magnetic field causes all liquids to exhibit optical rotation, usually in the same direction as that of the magnetizing current; this phenomenon is known as

the Faraday effect, and it may be expressed by the relation:

$$\theta = \rho t h$$

where θ is the total angle of rotation, t is the thickness of substance through which the light passes, and h is the magnetic field; the constant ρ is an intrinsic property of the substance, usually termed the Verdet constant (minutes of arc/cm/gauss). There have been some attempts to use the Verdet constant in studying the constitution of hydrocarbons by physical property correlation (Gruse and Stevens, 1960).

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CHAPTER

7

SPECTROSCOPIC METHODS

7.1. INTRODUCTION

The chemical composition of a feedstock, subject to the reservations mentioned in an earlier chapter (Chapter 2), has always been considered to be a valuable indicator of refining behavior. Whether or not it is the ultimate indicator of refining behavior remains to be seen and is audience dependent! More than likely, chemical composition studies truly complement physical property and physical behavior studies, and the true picture is a combination of all of these studies.

However, the chemical composition of a feedstock is represented in terms of compound types and/or in terms of generic compound classes, thus allowing the analytical chemist, the process chemist, the process engineer, and the refiner to determine the nature of the reactions. Hence, chemical composition can play a large part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed (Nelson, 1958; Gary and Handwerk, 1984; Ali et al., 1985; Wallace et al., 1988; Speight, 2000). However, proper interpretation of the data resulting from the composition studies requires an understanding of chemical structures, their significance, and an open mind!

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

Spectroscopic studies have played an important role in the evaluation of petroleum and of petroleum products for the last three decades, and many of the methods are now used as standard methods of analysis for refinery feedstocks and products. Application of these methods to feedstocks and products is a natural consequence for the refiner.

The methods include the use of *mass spectrometry* to determine the (1) hydrocarbon types in middle distillates (ASTM D-2425); (2) hydrocarbon types of gas oil saturate fractions (ASTM D-2786); (3) hydrocarbon types in low-olefin gasoline (ASTM D-2789); and (4) aromatic types of gas oil aromatic fractions (ASTM D-3239). *Nuclear magnetic resonance spectroscopy* has been developed as a standard method for the determination of hydrogen types in aviation turbine fuels (ASTM D-3701). *X-ray fluorescence spectrometry* has been applied to the determination of lead in gasoline (ASTM D-2599), the analysis of selected elements (nitrogen, sulfur, nickel, and vanadium) in water-borne oil (ASTM D-3327), the identification of chemicals in water (ASTM D-4763), as well as the determination of sulfur in various petroleum products (ASTM D-2622, ASTM D-4294).

Infrared spectroscopy is used for the determination of benzene in motor and/or aviation gasoline (ASTM D-4053), and ultraviolet spectroscopy is used for the evaluation of mineral oils (ASTM D-2269) and for determining the naphthalene content of aviation turbine fuels (ASTM D-1840).

Other techniques include the use of *flame emission spectroscopy* for determining trace metals in gas turbine fuels (ASTM D-3605) and the use of *absorption spectrophotometry* for the determination of the alkyl nitrate content of diesel fuel (ASTM D-4046). *Atomic absorption* has been used as a means of analysis of metals (ASTM D-1971, ASTM D-4698, ASTM D-5056), for measuring the lead content of gasoline (ASTM D-3237, IP 362), for the manganese content of gasoline (ASTM D-3831), as well as for determining the barium, calcium, magnesium, and zinc contents of lubricating oils (ASTM D-4628). *Flame photometry* has been used as a means of measuring the lithium/sodium content of lubricating greases (ASTM D-3340) and the sodium content of residual fuel oil (ASTM D-1318).

Nowhere is the contribution of spectroscopic studies more emphatic than in application to the delineation of structural types in the heavier feedstocks. This has been necessary because of the unknown nature of these feedstocks. One particular example is the *n.d.M. method* (ASTM D-3238) that is designed for the carbon distribution and structural group analysis of petroleum oils. Later investigators have taken structural group analysis several steps further than the *n.d.M.* method.

It is also appropriate at this point to give a brief description of other methods that are used for the identification of the constituents of petroleum (Yen, 1984).

Although very useful information can be provided about the composition of high-molecular-weight petroleum fractions by the right combination of separation and analytical methods, spectroscopic methods can also be applied to the problems of characterization and identification. For example, information about the nature of polar functional groups or the elucidation of the way vanadium and nickel are bound to the molecules is available from a variety of spectroscopy techniques as well as by use of a variety of chemical techniques (Chapter 8).

It is not intended to convey here that any one of these methods can be used for complete characterization and identification of the high-molecular-weight

petroleum constituents. Even though any one of these methods may fall short of complete acceptability as a method for the characterization of individual constituents of feedstocks, they can be used as methods by which an overall evaluation of the feedstock may be obtained in terms of molecular types. This is especially true when the methods are used in conjunction with each other.

In this chapter, an examination of the various spectroscopic and spectrometric techniques is presented as well as examples of the application of these techniques to studies of the chemical composition of petroleum, heavy oil, and bitumen.

7.2. INFRARED SPECTROSCOPY

Infrared spectroscopy is a well-established method that was developed for comparative, semiquantitative analysis leading to the present quantitative analysis (ASTM E-168, ASTM E-204, ASTM E-334, ASTM E-1252, IP 429; Bellamy, 1975; Nakanishi and Solomon, 1977; Sastri et al., 1995).

Infrared spectra are displayed either as percent transmittance or as absorptivity versus frequency (cm^{-1}). Transmittance (T), defined as the ratio of transmitted light over incident light, or percent transmittance ($100T$), usually shows more detail over the entire range and is generally the preferred display. Absorbance (A), on the other hand, is proportional to the concentration and is, therefore, used for quantitative measurements. Thus,

$$A = -\log_e(T)$$

It is more common now to record the apparent absorptivity, A_{app} ,

$$A_{\text{app}} = \log_{10}(T)$$

Therefore, at sufficiently low concentration,:

$$-\log_{10}(T)_v = cl\varepsilon_v$$

where v is the wavelength of the light, c is the sample concentration, l is the sample thickness (path length), and ε is the (apparent) molecular absorption coefficient at that wavelength. The true molar absorption coefficient is proportional to the natural logarithm of the transmittance.

Infrared spectroscopy is a simple procedure and provides quick information about the distribution of several structural and functional groups (Table 7.1). In combination with nuclear magnetic resonance spectroscopy, it will provide quick yet fairly detailed data on the distribution of carbon-hydrogen groups (Yen, 1973).

Table 7.1. Band Assignments in the Infrared Spectra of Petroleum Fractions

Band		
cm ⁻¹	μ	Assignment
3030	3.30	Aromatic C—H stretching
2920	3.42	Methyl C—H stretching
2880	3.47	Methylene C—H stretching
1735	5.76	Carbonyl C=O
1700	5.88	Carbonyl C=O
1600	6.25	C=C and C=O (hydrogen-bonded)
1465	6.83	C—H bending
1380	7.25	C—H bending in methyl groups
1130	8.85	Sulfur-oxygen functions
1020	9.80	Sulfur-oxygen functions ^a
865	11.56	
815	12.27	
760	13.16	
735	13.61	
		Aromatic C—H bending (out of plane)

^aAlso aromatic ethers.

However, in the context of high-molecular-weight petroleum fractions, conventional infrared spectroscopy yields information about the functional features of various petroleum constituents. For example, infrared spectroscopy will aid in the identification of imino (=N—H) and hydroxyl (—O—H) functions, as well as the nature of the various carbonyl (—C=O) functions.

In the older infrared spectroscopy, light is refracted by a prism or a grating and scanned by a moving slit that takes several minutes for one measurement. In *Fourier transform infrared (FTIR) spectroscopy*, the entire spectrum is obtained by an interferometer in a fraction of a second. Several hundred measurements can be taken in a matter of minutes and averaged by computer. This multiplexing leads to greatly increased (about 100-fold) sensitivity and precision over those achievable with dispersive instruments.

Thus, with the recent progress of Fourier transform infrared (FTIR) spectroscopy, quantitative estimates of the various functional groups can also be made. This is particularly important for application to the higher-molecular-weight solid constituents of petroleum (i.e., the asphaltene fraction) and for group-type analysis (Iob et al., 1996; Michon et al., 1997).

It is also possible to derive structural parameters from infrared spectroscopic data, and these are (1) saturated hydrogen-to-saturated carbon ratio; (2) paraffinic character; (3) naphthenic character; (4) methyl group content; and (5) paraffin chain length.

In conjunction with proton magnetic resonance (see next section), structural parameters such as the fraction of paraffinic methyl groups to aromatic methyl groups can be obtained.

The newer diffuse reflectance infrared (DRIR) techniques (Fuller and Griffiths, 1978; Christy et al., 1989) seem to give spectra equally as good as those obtained in conventional ways from solutions in cells or from potassium bromide (KBr) pellets. Another synonym for this technique is DRIFT (for diffuse reflectance infrared Fourier transform).

The sample is deposited from solution onto finely ground potassium bromide in a small cup that is placed into a diffuse reflectance accessory after removal of the solvent in a vacuum oven. A related technique, variable angle specular reflectance, allows rotation of the sample holder for optimization.

Increased resolution by band narrowing techniques (Wang and Griffiths, 1985; Chen et al., 1985) in conjunction with reference spectra allows the distinction of methylene (CH_2) groups next to other groups such as alkyls, aromatic rings, carbonyls, or alkoxyl groups. Carbon-hydrogen (CH_n) groups and aromatic carbon can be identified, measured, and compared. The ratio of the band at 1602 cm^{-1} (aromatic C—C stretching) to that at 2920 cm^{-1} [aliphatic hydrogen-carbon stretching in methylene groups (β or further away from the aromatic ring)] is a good relative measure for the aromaticity of a sample.

Fourier transform infrared spectroscopy is sufficiently sensitive that it can be used for detection in high-performance liquid chromatography (HPLC) and even in gas chromatography (GC) and supercritical fluid chromatography (SFC) (Norton et al., 1991).

Band assignments (Table 7.1) for infrared spectra were established several decades ago. Resolution enhancement by Fourier self-deconvolution (band narrowing) led to the recognition and distinction of bands that previously could not be separated. Examples of such new assignments are methyl (CH_3) groups next to aromatic rings (2948 cm^{-1}) and next to alkyl groups (2960 cm^{-1}), methylene (CH_2) groups (together with some methyl groups) next to aromatic rings (2916 cm^{-1}) and in aliphatic chains (2926 cm^{-1}), methylene groups next to an alkoxy function (2928 cm^{-1}) and next to a carbonyl group (2933 cm^{-1}); and methine (CH) groups in unspecified environments (2905 cm^{-1} and 1897 cm^{-1}). The rocking vibration band of methylene groups in straight aliphatic chains varies slightly with their length. For *n*-pentyl groups, it is located at 726 cm^{-1} , and with longer chains, it shifts to lower frequencies until it stabilizes at 720 cm^{-1} for chains with more than nine carbon atoms.

In the analysis of the high-molecular-weight petroleum constituents, infrared spectroscopy has been mostly used for measuring oxygen- and nitrogen-containing groups and for evaluating shifts in certain bands caused by aggregation or other interactions such as carboxylic acids, phenols, carbazoles, cyclic amides, as well as pyridine and acridine variants among the bases (Petersen, 1967; McKay et al.,

1975, 1976; Moschopedis and Speight, 1977; Green et al., 1985; Jacobson and Gray, 1987).

In the lower-boiling petroleum fractions, parts of the hydrocarbon skeleton can be assessed by infrared spectroscopy. Specifically, the alkyl substitution of aromatic rings can be determined from the out-of-plane carbon-hydrogen deformation bands (Jokuty and Gray, 1991).

7.3. NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance has frequently been used for general studies of hydrogen types in petroleum and petroleum products (ASTM D-4808, IP 392) as well as for the structural studies of petroleum constituents (ASTM E-386; see also Bouquet and Bailleul, 1982; Hasan et al., 1989; Speight, 1994). The technique has recently been adapted to measure the hydrogen content of fuels and other petroleum products (ASTM D-3701; ASTM D-4808 IP 338) (see also Chapter 4). In fact, *proton magnetic resonance* (PMR) studies (along with infrared spectroscopic studies) were, perhaps, the first studies of the modern era that allowed structural inferences to be made about the polynuclear aromatic systems that occur in the high-molecular-weight constituents of petroleum.

Thus nuclear magnetic resonance (NMR) methods have gained a prominent place in the compositional and structural analysis of petroleum fractions (Speight, 1994). In its basic applications, NMR is fast and relatively inexpensive. Because of its convenience, speed, and greater wealth of detailed information, particularly from ^{13}C -NMR, it has displaced the *n-d-M* and related methods (Chapter 11) in most laboratories. NMR directly measures aromatic and aliphatic carbon as well as hydrogen distributions. Beyond these results, both C and H in various structural groupings in a molecule can be determined.

Proton (^1H) and carbon-13 (^{13}C) nuclei are the most common ones used in NMR spectroscopy; nitrogen (^{15}N and ^{14}N) and sulfur (^{33}S) have been used on occasion with petroleum fractions for special applications. This section focuses on the regular NMR techniques (^1H and ^{13}C) for the structural group analysis of petroleum fractions.

Proton magnetic resonance has been widely used in the structural analysis of petroleum fractions. It is a relatively inexpensive technique, that allows measurement of hydrogen atoms in aromatic and aliphatic groups, even allowing differentiation between hydrogen attached to next to an aromatic ring (α -position) and those farther removed from the ring. Atoms in single-ring and multiring aromatic compounds as well as those in olefinic locations can also be identified.

Only a small amount (<10 mg) of the sample is required, dissolved in a solvent such as deutero-chloroform, contained in a glass tube of 5-mm diameter and placed in a highly homogeneous magnetic field where it is surrounded by one or more

coils. The coils serve to subject the sample to a weak radio-frequency (rf) field. The hydrogen nuclei of the sample can be visualized as magnets, and when the radio frequency is equal to the processing frequency, resonance occurs between the two and the spin resonance is detected by a receiver coil. The position of a sample resonance with that of tetramethylsilane (TMS) as a reference difference is reported as *chemical shift* δ , which is a dimensional number that is expressed in terms of parts per million (ppm) difference from the reference (TMS) (Tables 7.2 and 7.3) (Bartle et al., 1979b; Snape et al., 1983; Cookson and Smith, 1987; Netzel, 1987).

Quantitative accuracy of proton magnetic resonance for aromatic and aliphatic hydrogen is about 1% for distillates and 2–3% for residua; that for the distinction of aliphatic hydrogen atoms α to an aromatic ring from those β and farther away from the ring is somewhat lower. Methyl (CH_3), methylene (CH_2), and methine (CH) hydrogen can ordinarily not be distinguished except for methyl hydrogen γ or farther away from aromatic rings. Even this methyl peak is sometimes difficult to quantify because of interference by naphthenic methine and methylene hydrogen.

Protons attached to single-ring and multiring aromatic compounds can usually be distinguished with reasonable accuracy, especially when the sample concentration is 2% or less. At such low concentrations, the dividing line between these protons is at 7.25 ppm (Cookson and Smith, 1987). In the spectra of samples with high boiling point, much of the detail is lost and differentiation between group types is difficult.

Thus, in general, the proton (hydrogen) types in petroleum fractions can be subdivided into three types (Brown and Ladner, 1960):

1. aromatic ring hydrogen;
2. aliphatic hydrogen adjacent to an aromatic ring; and
3. aliphatic hydrogen remote from an aromatic ring

or into five types (Yen and Erdman, 1962):

1. aromatic hydrogen;
2. substituted hydrogen next to an aromatic ring;
3. naphthenic hydrogen;
4. methylenic hydrogen; and
5. terminal methyl hydrogen remote from an aromatic ring.

Other ratios are also derived from which a series of structural parameters can be calculated.

However, it must be remembered that the structural details of the carbon backbone obtained from proton spectra are derived by inference but protons at peripheral positions can be obscured by intermolecular interactions. This, of course, can

Table 7.2. Proton Signal Assignments in Organic Compounds

Signal τ		Assignment
2.00	N—H	Pyrrole
2.19	α -H	Naphthalene
2.54	β -H	Naphthalene
2.58	2-H	Furan
2.73	Ar—H	Benzene
2.81	Ar—H	Thiophene
2.89	Ar—H	Ethylbenzene
2.91	Ar—H	Toluene
3.03	Ar—H	Tetralin
3.36	Ar—H	Mesitylene
4.43	Olefinic H	Cyclohexene
6.08	α -CH ₂	Diphenylmethane
6.19	CH ₂	Fluorene
7.09	α -CH ₂	Indane
7.13	α -CH ₂	Dibenzyl
7.30	α -CH ₂	Tetralin
7.38	α -CH ₂	Ethylbenzene
7.66	CH ₃	Toluene
7.77	CH ₃	<i>o</i> -Xylene
7.86	CH ₃	Durene
7.96	β -CH ₂	Indane
8.04	Allylic CH ₂	Cyclohexene
8.21	CH ₂	Adamantane
8.27	β -CH ₂	Tetralin
8.30	3-CH ₂	2-Phenylbutane
8.40	H(eq.)	<i>trans</i> -Decalin (strong)
8.46	CH ₂	Methylcyclohexane
8.47	CH ₂	Cycloheptane
8.47	CH ₂	Cyclooctane
8.49	CH ₂	Cyclopentane
8.54	CH ₂	Cyclohexane
8.59	CH ₂	<i>cis</i> -Decalin
8.75	CH ₂	<i>n</i> -Hexane
8.75	CH ₂	<i>n</i> -Octane
8.77	1-CH ₃	2-Phenylbutane
8.80	CH ₃	Ethylbenzene
9.08	CH ₃	Methylcyclohexane
9.10	CH ₃	<i>n</i> -Hexane
9.11	CH ₃	<i>n</i> -Heptane
9.12	CH ₃	<i>N</i> -Octane
9.12	H(ax.)	<i>trans</i> -Decalin (weak)
9.20	4-CH ₃	2-Phenylbutane
10.00	CH ₃	Tetramethylsilane

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Table 7.3. General Hydrogen Group Assignments in the Proton Magnetic Resonance Spectra of Petroleum Fractions

Symbol	Range τ	Center τ	Band		Assignments ^a	
					Major	Minor
H _A	1.50–3.70	2.60		Aromatic protons		OH in phenols NH in pyrroles
H _{α}	6.60–8.30	7.45	α -Methyl α -Methylene α -Methine		Paraffinic	
H _N	7.80–8.60	8.20	Methylene Methine <i>cis</i> -Peripheral Bridge Methine		Naphthenic	β -Methyl paraffinic
H _{My}	8.20–9.10	8.65	Methylene other than α - or β -paraffinic			β -Methylparaffinic trans- peripheral bridge methine-naphthenic
H _{Me}	8.60–9.50	9.05	Methyl other than α - or β -paraffinic			<i>trans</i> -Peripheral bridge methine-naphthenic

^aThe letters α and β indicate positions relative to an aromatic ring.

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cause errors in the ratios that can have a substantial influence on the outcome of the calculations (Ebert et al., 1987; Ebert, 1990).

It is in this regard that *carbon-13 magnetic resonance* (CMR) can play a useful role. Because carbon magnetic resonance deals with analyzing the carbon distribution types (Table 7.4; Altgelt and Boduszynski, 1994), the obvious structural parameter to be determined is the aromaticity, f_a . A direct determination from the various carbon type environments is one of the better methods for the determination of aromaticity (Snape et al., 1979). Thus, through a combination of proton and carbon magnetic resonance techniques, refinements can be made on the structural parameters and, for the solid-state high-resolution CMR technique, additional structural parameters can be obtained (Weinberg et al., 1981).

The basic instrumentation for carbon-13 magnetic resonance is the same as that for proton magnetic resonance except that there are two radio frequency fields orthogonal (at right angles) to the main magnetic field, one for observing the carbon-13 nuclei and the other for decoupling the proton nuclei. The low abundance of carbon-13 isotopes (1.1%) and the lower gyromagnetic ratio of the carbon-13 nucleus make the signal weaker by more than two orders of magnitude, and, moreover, the nuclei have longer relaxation times. The effect is that, even with Fourier

Table 7.4. Carbon Assignments in ^{13}C Magnetic Resonance Spectroscopy

Peak No.	Chemical Shift (ppm)	Assignment
1	14.1–14.4	ω CH ₃
2	19.3–20.4	γ, δ CH ₃ α to CH
3	22.6–22.8	ϵ^+ CH ₂ next to CH ₃
	18–24	ϵ CH ₃ next to CH at end of chain
4	24.4–24.65	CH ₃ on naphthenic groups
5	24.8–25.1	ϵ^+ CH ₂ β to two CH groups
6	28.08–28.14	γ CH ₂ β to two CH groups
7	29.4–30.3	CH α to two terminal CH ₃ groups
a	29.5	γ^+ CH ₂ in long chains away from branch points
b	30.0	γ CH ₂ in long chains away from branch points
8	31.8–32.5	δ CH ₂ in long chains away from branch points
9	32.4–33.2	ϵ^+ CH ₂ 2 C removed from CH ₃
10	37.2–37.3	CH in chain next to CH ₃ (methyl branch)
11	37.5–37.7	δ^+ CH next to CH ₃ (isolated methyl branch)
12	39.3–39.6	ϵ^+ CH ₂ next to CH in chain far from end
		ϵ^+ CH ₂ next to CH chain near end

transform (FT) data acquisition, carbon-13 magnetic resonance measurements can take hours to perform.

In contrast to proton magnetic resonance spectroscopy, the peak areas arising from the carbon-13 nuclei in different molecular positions ordinarily are not proportional to their concentration. Quantitative measurements require that two effects must be overcome: (1) the different relaxation times of the carbon-13 nuclei in different chemical groups, and (2) the nuclear Overhauser enhancement (NOE). The latter effect refers to the rise in signal intensity when C—H coupled protons are saturated by the decoupling field.

One way to do this is to add a small amount of a paramagnetic relaxation reagent, such as trisacetylacetonechromium(III) [Cr(AcAc)₃], which changes the dominant relaxation mechanism into one involving the interaction between unpaired electrons and ^{13}C nuclei. It also reduces the long relaxation times of some carbons, thus taking care of the first of the two detrimental effects.

In its simplest form, carbon-13 magnetic resonance can distinguish between aliphatic and aromatic carbon (Bartle et al., 1979a). In the aliphatic region of petroleum ^{13}C -NMR spectra, several sharp peaks stand out and are used for quantitative evaluation (Bartle et al., 1979a, 1979b; Netzel et al., 1987; Cookson and Smith, 1985; Breitmaier and Voelter, 1987; Thiel and Gray, 1988; Sastri et al., 1995).

The most prominent peak is usually that at 29.7 ppm. It is attributed to methylene (CH_2) carbon atoms in long alkyl chains, positioned four or more carbons ($>\gamma$) away from an aromatic ring and from terminal methyl CH_3 groups.

Normally, the absorption of 29.5–30.3 ppm gives an estimation of the amount of carbon atoms in long alkyl chains ($>\text{C}_5$). Because this band represents methylene (CH_2) groups two or more carbons away from an aromatic ring and a terminal group, there must be four more carbons per chain than indicated by the area under these peaks. The *number of long chains* (n_{CH_2}) can be estimated from the peaks at 14.2 ppm ($\omega\text{—CH}_3$) and at 28.1 ppm (CH_2) next to a terminal branch point, i.e., a methine (CH) group. On the one hand, the peak at 14.2 ppm gives results too high for this purpose because it also indicates CH_3 groups from chain branches. Subtracting half of the 37.6-ppm peak area (CH_2 next to CH groups inside a chain) corrects for this feature. On the other hand, the peak at 14.2 ppm does not cover twin CH_3 groups (as in an isopropyl group.). This is why the 28.1 peak (CH next to 2 terminal methyl groups is needed. Thus

$$n_{\text{CH}_2\text{long chains}} = A(14.2) - 1/2A(37.6) + 1/3A(28.1)$$

The number of methylene groups in long chains is the sum of the by the peak at 29.7 ppm, the number of methylene groups at the two ends, i.e., six times the number of long chains for each of the two ends (Fig. 5.8), and the number close to branch points inside the chain, namely, those next to them and one carbon atom removed, on both sides of the CH group. Thus the total numbers is:

$$n_{\text{CH}_2} = C(29.7) + 6n_{\text{CH}_2\text{long chains}} + 4C(37.6)$$

The number of methine (CH) groups in long chains can be estimated from the absorbance at 37.6 ppm and at 39.5 ppm. The peak at 37.6 ppm represents methylene groups next to methane carbon and thus does not represent a direct measurement of the methane groups. Thus:

$$n_{\text{CHlong chains}} = 1/2C(37.6) + C(39.5)$$

The methyl groups give rise to at least four peaks in carbon-13 spectra, namely, the peaks at 11.5, 14.2, 19.5, and 22.7 ppm. The peak 22.7 ppm represents twin methyl groups as in an isopropyl group, and it also has a contribution from a methylene group next to a methyl group and does not need to be represented again by a contribution to the equation from the peak at 14.2 ppm. Thus:

$$n_{\text{CH}_3\text{long chains}} = C(11.5) + C(19.5) + C(22.7)$$

The final estimate for carbon atoms in long chains is then the sum of the three types. The average length of long chains derives from dividing the number of carbon atoms in long chains by the number of long chains, remembering, of course, that averages derived from magnetic resonance spectra can be very misleading if the data are interpreted too literally (Speight, 1999).

The methyl group (CH_3) gives rise to several peaks depending on its position in the molecule. A peak at 14.2 ppm signals such a group positioned at the end of an unbranched chain segment of at least two or three methylene (CH_2) groups. A methyl group next to a branch point (methine group, CH) at the end of a chain with at least two methylene groups produces a peak at 22.7 ppm. Farther away from the end of the chain, such a group gives a peak at or near 19.8 ppm. The methyl group at the end is also affected by these branch points (Fig. 5.8).

Naphthenic carbon in high-molecular-weight petroleum fractions usually occupies so many slightly different positions that the peaks are unresolved and form a broad hump in the range 25–60 ppm, under the generally well-resolved paraffinic peaks.

The evaluation of the hump is the only direct method for the determination of naphthenic methylene and methane (CH_n) groups. However, its measurement may not always be reliable. In very high-boiling petroleum samples, such as asphaltenes, the paraffinic resonance may be only partly resolved. Although this leads mainly to broader peaks, the overlap may in some cases add to the hump and, thus, cause erroneously high results for naphthenic carbon. The aromatic region of the ^{13}C -NMR spectrum can be evaluated by conventional integration of the peaks due to the main aromatic group types.

Thus proton and carbon-13 magnetic resonance spectroscopic techniques offer potential information about the molecular types in the nonvolatile fractions of petroleum. The techniques have, by the application of the estimation of peak areas and further application of mathematical methods, been used to obtain information about *structural parameters* that are then converted to *average structures*.

In most cases, the average structure of such complex mixtures as petroleum fractions is not the same as a representative structure. As already noted, average structures derived from magnetic resonance spectra can be very misleading if the data are interpreted too literally (Speight, 1999). Even though the average structures may always be questioned, one must also treat with some caution the structural parameters because they have been derived using assumptions that themselves are subject to debate.

7.4. MASS SPECTROMETRY

Mass spectrometry furnishes the molecular weight and chemical formula of compounds and their relative amounts in a mixture and offers nondestructive examination of the sample (ASTM D-2425, ASTM D-2650, ASTM D-2786, ASTM

D-2789, ASTM D-3239, ASTM E-1316.). The technique can also provide important information about their molecular structure. The earliest and most common type of mass spectrometry, electron impact mass spectrometry (EI-MS), gives a fragmentation pattern displaying both parent ion peaks and fragment ion peaks, characteristic of each molecular type.

Fragmentation is frequently used to differentiate between isomers of pure compounds and of molecules in fairly simple mixtures. However, it is usually avoided with such complex samples as high-molecular-weight petroleum fractions, which are composed of such a multitude of closely related compounds that their fragmentation patterns are nondistinctive and cannot be readily interpreted.

Mass spectrometry can play a key role in the identification of the constituents of feedstocks and products either in the laboratory or on-line (ASTM D-2425; ASTM D-2786; ASTM D-2789; ASTM D-3239; see also Acczel, 1989; Cook et al., 1999). The principal advantages of mass spectrometric methods are (1) high reproducibility of quantitative analyses; (2) the potential for obtaining detailed data on the individual components and/or carbon number homologues in complex mixtures; and (3) a minimal sample size required for analysis. The ability of mass spectrometry to identify individual components in complex mixtures is unmatched by any modern analytical technique, with perhaps the exception of gas chromatography.

However, there are disadvantages arising from the use of mass spectrometry and these are (1) the limitation of the method to organic materials that are volatile and stable at temperatures up to 300°C (570°F) and (2) the difficulty of separating isomers for absolute identification. The sample is usually destroyed, but this is seldom a disadvantage.

Nevertheless, in spite of these limitations, mass spectrometry does furnish useful information about the composition of feedstocks and products even if this information is not as exhaustive as might be required. There are structural similarities that might hinder identification of individual components. Consequently, identification by type or by homologue will be more meaningful because similar structural types may be presumed to behave similarly in processing situations. Knowledge of the individual isomeric distribution may add only a little to an understanding of the relationships between composition and processing parameters.

Mass spectrometry should be used discriminately where a maximum amount of information can be expected. The heavier nonvolatile feedstocks are, for practical purposes, beyond the useful range of routine mass spectrometry. At the elevated temperatures necessary to encourage volatility, thermal decomposition will occur in the inlet, and any subsequent analysis would be biased to the low-molecular-weight end and to the lower-molecular-weight products produced by the thermal decomposition.

High-voltage electron impact mass spectrometry can cause repeated fragmentation of daughter ions. Considering the repeated fragmentation of even the simplest hydrocarbons and the fact that the higher-molecular-weight fractions of petroleum

contain such a broad range of molecular weight species (Chapter 12), the patterns obtained from petroleum fractions are so complex as to almost defy interpretation. Thus nonfragmenting mass spectrometric methods are preferred.

For high-molecular-weight petroleum fractions, the use of *nonfragmenting mass spectrometry (NF-MS)* methods is now preferred. These methods, also called *soft ionization* methods, produce predominantly parent ion (molecular ion) peaks and thus much simpler spectra than methods producing fragments. By rendering the molecular weight and reasonably well the abundance of each compound in a sample, nonfragmenting mass spectrometry also can be used to determine the molecular weight distribution, i.e., the molar mass profile of a sample.

Indeed, the great advantage of nonfragmenting mass spectrometry is the relative simplicity of the spectra. A disadvantage is the relatively low signal intensity of the ions. With *low-voltage electron impact ionization*, the number of parent ions formed increases rapidly as the ionizing voltage increases above the ionizing potential of the molecules in the sample. Thus higher voltage gives a more intense signal (up to about 20–40 eV, depending on compound type). However, the higher ionizing voltage transfers more energy to the sample molecules and causes fragmentation to increase. The surplus energy transferred to the molecule in excess of the ionizing potential is equilibrated and dissipated in various ways, for example, by increasing the internal energy of the molecule or by breaking atomic bonds.

Thus the challenge in nonfragmenting mass spectrometry is to maximize the number of parent ions and, at the same time, maintain the number of fragment ions at acceptable levels.

Paraffins are highly susceptible to fragmentation; an ionizing voltage high enough to generate a good parent ion spectrum also breaks many (paraffinic) carbon-carbon bonds, producing a significant number of fragment ions.

Among the most important nonfragmenting mass spectrometric techniques are field ionization mass spectrometry (FIMS), field desorption mass spectrometry (FDMS), chemical ionization mass spectrometry (CIMS), and low-voltage (10–20 eV) electron impact mass spectrometry (LVEI-MS). A particularly powerful version of electron impact mass spectrometry is high-resolution electron impact mass spectrometry (HR-LEVI-MS or LVRH-MS). All of these are “soft” ionization techniques, designed to generate *cold* ions of such low excess energy that they do not undergo fragmentation to any great extent, in contrast to the *hot* ions generated by conventional electron impact ionization (70–100 eV). With soft ionization methods, a compromise must be found between low fragmentation and sufficiently high sensitivity. Unfortunately, samples rich in aliphatic hydrocarbons are hard to keep completely from fragmenting, but most other compound types, especially aromatic compounds, yield clean parent ion spectra.

Field ionization mass spectrometry shows extremely low fragmentation because the ionization process imparts little excess energy to the formed ion. This is crucial when ionizing saturates. Both low-voltage electron impact (LVEI) and chemical

ionization (CI) transfer more excess energy than field ionization mass spectrometry, leading to higher levels of fragmentation with saturates. As long as the analyte is volatile, the field ionization mass spectrometry experiment is not sample limited. That is, additional sample can be vaporized as needed to obtain the required signal-to-noise ratio. Field desorption mass spectrometry (FDMS) can be considered a special form of electron impact mass spectrometry (EIMS) where the sample material is placed on the ionizing surface of the probe before insertion into the sample chamber of the mass spectrometer. It is, however, sample limited and subject to experimental artifacts not normally present in electron impact mass spectrometry.

In the electron impact mass spectrometry technique, the emitting surface is a cathode consisting of an array of sharp tips on a support such as a wire, a grid, or a razor blade. This surface is located very close to the anode. The combination of an extremely small radius of curvature of the tips, the short distance, and the high electric field creates a very high field gradient. The sample is introduced to this field gradient by evaporation and diffusion from a heated surface nearby.

Field desorption mass spectrometry is a special form of field ionization mass spectrometry. The cathode is the same, but here it is coated with the sample before it is placed in the mass spectrometer source. This eliminates the need to evaporate the sample and any losses on transport to the cathode. Instead, the ions are desorbed directly from the solid sample. The emitter is heated to the point where the sample melts and can be drawn by the surface tension to the tip where the molecules are converted to ions. As the ions are ejected from the surface into the mass spectrometer, more sample molecules can replace them at the tip. In this way, labile molecules can be handled without significant fragmentation, and even conventionally nonvolatile samples can be run. Thus the method is especially suitable for the high-molecular-weight fractions of petroleum residua. Because of the low thermal energy to which the sample molecules are exposed, the total excess energy in this process is minimal. Thus, field desorption mass spectrometry is an even milder method than field ionization mass spectrometry and produces less fragmentation.

Low-voltage mass spectrometry is a soft electron impact mass spectrometric method using 10–16 eV instead of the conventional 70–100 eV, thereby avoiding or greatly mitigating fragmentation for petroleum constituents. The sensitivity of the method is about the same as that of field ionization mass spectrometry, but compared to regular electron impact mass spectrometry, it is 10–100 times lower, and, therefore, the data acquisition time needed for the same signal-to-noise ratio increases proportionally.

Chemical ionization mass spectrometry (CI-MS), another soft method, has been used only occasionally for petroleum samples (Dzidic et al., 1991). In this method, a relatively high-pressure (0.1–1 Torr) reagent gas (e.g., methane, *n*-butane, *iso*-butane) is ionized and allowed to contact the sample. At such pressures, the reagent

ions undergo many collisions that help them lose excess energy left after ionization. The ions also exchange charges during collision with one another and with the sample molecules. The latter is the desired reaction, and the methods works best when the sample molecules retain the charge better than the reagent molecules.

Fast atom bombardment mass spectrometry (FAB or FABMS) is a method for special applications, namely, for polar, high-boiling samples when some fragmentation is desired for identification.

In fast atom bombardment mass spectrometry (FAB-MS) the sample is dissolved in a high-boiling polar liquid matrix (such as glycerol or triethanolamine) and spread on a plate. Rare gas molecules (e.g., Xe or Ar) are ionized, accelerated, focused at the sample, and stripped of their charge before they hit their target. The impact of uncharged atoms sputters small amounts of the matrix and sample off the sample plate. The liquid matrix evaporates, liberating charged sample ions, which are now propelled by the accelerating voltage into the mass spectrometer.

The method produces substantial amounts of fragments and rarely works for neutral compounds, two disadvantages for our purpose. Other problems and interferences with fast atom bombardment mass spectrometry are that the matrix material is ionized along with the sample and that both sample and matrix material may form cluster ions that complicate the spectrum.

The most useful application of *low-voltage mass spectrometry* is in combination with high-resolution conditions. The method not only provides a parent ion spectrum (for fractions free of saturates) as does FIMS or FDMS, but it can distinguish between molecules of equal nominal mass.

For high-resolution mass spectrometers, precise standardization of operating conditions is even more important for quantitative measurements than for regular mass spectrometers. Generally, the higher the resolution, the weaker the signal and the longer the data acquisition time. Special mass standards, mostly chlorinated hydrocarbon petroleum fractions, are used for mass calibration. The parent petroleum fractions guarantee a complete mass sequence that is needed for the large number of heterocompound peaks. Even with such a standard there will still be several heterocompound peaks between each pair of hydrocarbon peaks. The chlorocompounds are preferred because of their higher sensitivities at the low ionization voltage compared to those of the fluorinated standards common with regular electron impact mass spectrometry.

Gas chromatography coupled with mass spectrometry (GC-MS) is a powerful method for petroleum distillates. Heavy petroleum fractions (345–450°C, 650–850°F) are usually first separated by liquid chromatography into compound class fractions before application of gas chromatography that separates the sample by boiling point (Chapter 10). Mass spectrometry, used as a detection method, gives the molecular weight and, with fragmenting ionization, the compound type of each peak (Lai and Song, 1995; Boehm et al., 1997).

Petroleum samples boiling higher than about 450°C (850°C), other than well-separated narrow fractions, are too complex and high boiling for gas chromatography. In these cases, nonfragmenting mass spectrometry should be combined with liquid chromatography instead of gas chromatography.

Very high-boiling samples (>650°C, >1200°F) may not be seen with the same sensitivity as lower-boiling constituents by most mass spectrometric methods. For these cases, mass spectrometric methods not limited by volatility are now available. For example, FDMS, laser desorption (LS), fast atom bombardment (FAB), and electrospray (ES) techniques can be applied to very large (polar) molecules, even of several thousand molecular weight. However, because FAB and ES work only with highly polar, easy-to-ionize compounds, their application to petroleum fractions may be limited.

Liquid chromatography-mass spectrometry is more difficult than gas chromatography-mass spectrometry (Covey et al., 1986) insofar as the solvent needs to be removed before the eluate can be processed by the mass spectrometer. After solvent removal, the sample passes through the ionization chamber of the mass spectrometer where the sample is vaporized and can be ionized by any method, including fast atom bombardment and electron impact.

One of the applications of mass spectrometry is group-type mass spectrometry. The method uses fragment patterns and sets of empirical relations to sort the contributions from different molecules to certain selected peaks and to reconstruct the molecular distribution from these peak areas.

The ASTM D-2786 method, for instance, measures the concentration of eight compound types; paraffins, naphthenes with one to six rings, and mono-aromatics in the saturates fractions. The application of this method is restricted to petroleum fractions having an average carbon number between 16 and 32. The ASTM D-3239 mass spectrometric group-type method is used to determine aromatic compound types present in chromatographic fractions of aromatics separated from vacuum gas oils. Other ASTM group-type methods determine various aliphatic and aromatic compound types in middle distillates (ASTM D-2425, ASTM D-2625).

Mass spectrometric group-type methods are fast and relatively cheap, and they require a sample of only a few milligrams. However, they have their limits. They are restricted to samples free of olefins and, ordinarily, with less than 2–5% S, N, or O compounds and in some cases, with much more stringent limits. Other restrictions, for example, to certain boiling (and MW) ranges also apply, depending on the method. Furthermore, only those compound types are considered in the calculation for which results are given in the output. If any other compound types are present in the sample to any large degree, which may easily be the case, major errors may result.

The mass spectrometric group-type analysis makes use of average fragmentation patterns specific to the different compound types, that is, to certain groups of

molecular structures. But the masses, as well as the abundances, of fragment ions are characteristic of the specific parent molecule.

The sum of all of the peaks gives the average distribution of the parent molecules. Generally, a limited set of peaks of a molecule is selected for evaluation. Calibration ensures that the system is operating in a reproducible fashion and a response factor matrix approach is used for quantitative measurement and to compensate for overlaps in fragmentation.

Selected fragment peak intensities within the homologous series of compound types are added together, and the sums are evaluated with a matrix of response factors to give the concentration of each compound type in the sample.

Mass spectrometric group-type analyses can be expected to have errors in the order of up to 20%. However, *relative* changes are ordinarily reported with better accuracy.

7.5. ULTRAVIOLET SPECTROSCOPY

The ultraviolet-visible (UV-Vis) spectrum, although not as specific for chemical group types as infrared spectroscopy and nuclear magnetic resonance spectroscopy, can distinguish between aromatic compounds with different ring numbers and configurations (ASTM D-1840, ASTM D-2269). The patterns are not distinct enough to recognize or distinguish these compounds in complex mixtures, but they can be useful for their identification in narrow fractions.

Ultraviolet-visible spectroscopy (ASTM E-169) can be used as a detector for the fractionation of petroleum samples, for example, for the chromatographic separation and/or identification of aromatics by ring number, especially in combination with a technique such as liquid chromatography (Speight, 1986). Thus ultraviolet-visible spectroscopy lends itself to studies of refining processes as an on-line detector.

7.6. X-RAY DIFFRACTION

X-ray diffraction had been used (Yen et al., 1961) for the determination of the fraction of aromatic carbon (f_a) in petroleum constituents. This ratio can also be conveniently and precisely obtained by carbon-13 nuclear magnetic resonance spectroscopy as well as by infrared spectroscopy. The determination of the fraction of carbon that is aromatic may be in error (Ebert, 1990) because X-ray diffraction data can be very misleading (Ebert et al., 1984), especially when the data are used to translate geometric data—measurements of (aromatic) sheet diameter—into structural information. On the one hand, not all aromatic atoms contribute to the

stack diameter seen by X-ray diffraction, whereas, on the other hand, nonaromatic atoms such as hydroaromatic carbons and other substituents on aromatic rings may contribute to the diffraction pattern. Thus the interpretation of these measurements is quite arbitrary.

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy are tools for the investigation of the immediate chemical environment of X-ray absorbing elements such as metals and sulfur (Goulon et al., 1984). X-ray absorption near-edge structure and x-ray photoelectron spectroscopy (XPS) have been applied to the determination of sulfur compounds as well as nickel and vanadium in petroleum samples described by (Kelemen et al., 1990a, 1990b; Waldo et al., 1991)

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CHAPTER

8

CHEMICAL METHODS

8.1. INTRODUCTION

As noted in other chapters, in the early days of petroleum processing, the need to understand the character and behavior of petroleum in the detail that is currently required did not exist. Refining involved distillation of the valuable kerosene fraction, which was then sold as an illuminant. After the commercialization of the internal combustion engine, the desired product became gasoline, and it was also obtained by distillation. Even when crude oil that contained little natural gasoline was used, cracking (i.e., thermal decomposition with simultaneous removal of distillate) became the modus operandi.

However, with the startling demands on the petroleum industry during and after World War II and the emergence of the age of petrochemicals and plastics, the petroleum industry needed to produce materials that were not even considered as products in the decade before the war. Thus petroleum refining took on the role of technological innovator as new and better processes were invented and advances in the use of materials for reactors were developed. In addition, there arose the necessity to find out more about petroleum so that refiners might be able to enjoy the luxury of predictability and plan a product slate that was based on market demand—a difficult task when the character of the crude oil was unknown! The idea that petroleum refining should be a *hit or miss* affair was not acceptable.

The processing of petroleum requires not only knowledge of its chemical and physical properties but also knowledge of its chemical and physical reactivity. The former is dealt with in this chapter; the latter, because of the structure of petroleum, is dealt with elsewhere in this book (Chapter 14). Because petroleum varies markedly in its properties and composition according to the source, it also varies in its chemical and physical reactivity. Thus knowledge of petroleum reactivity is required for optimization of existing processes as well as for the development and design of new processes.

For example, valuable information can be obtained from the true boiling point (TBP) curve (Chapter 5), which is a function of percent weight distilled and temperature, that is, a boiling point distribution (Fig. 8.1). However, the boiling range does not convey much detail about chemical reactivity of crude oil. In addition to the boiling point distribution, it is possible to measure bulk physical properties,

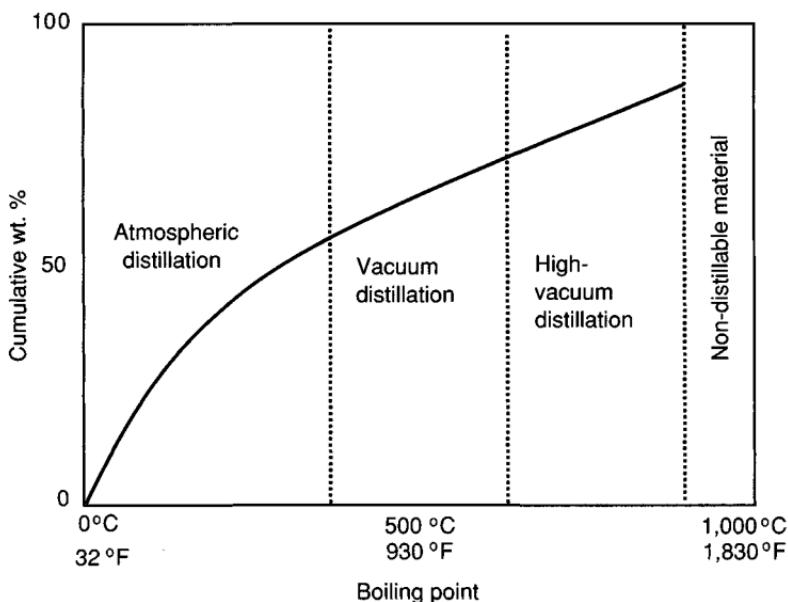


Figure 8.1. True boiling point curve (distillation profile) for petroleum.

such as specific gravity and viscosity, that have assisted in the establishment of certain empirical relationships for petroleum processing from the TBP curve. Many of these relationships include assumptions that are based on experience with a range of feedstocks. However, the chemical aspects of refining feedstocks that contain different proportions of chemical species emphasize the need for more definitive data that would enable more realistic predictions to be made of crude oil behavior in refinery operations.

The history of analysis of the chemical constituents in petroleum started over 100 years ago, when, in 1865, several aromatic hydrocarbons were identified as constituents of petroleum. Identification of individual constituents of petroleum has continued, and the rapid advances in analytical techniques have allowed the identification of large numbers of petroleum constituents. At this time, the major chemical types of compounds that exist in crude oil have been identified, and many members of the various homologous series have been separated or conclusively identified by various techniques (Chapter 2). This indicates a wealth of organic compounds that are either resistant to mild hydrogenation (such as paraffins) or reactive under destructive hydrogenation conditions.

As the boiling points of petroleum fractions increase, the complexity of the constituents in these fractions also increases, and the differences in chemical reactivity between the main classes of constituents may become less pronounced. Nevertheless, the properties of any material are dictated by its chemical composition, and,

once the chemical composition of a material has been established, it becomes possible to correlate composition and properties. Petroleum is no exception to this generality.

It is generally recognized that crude oils are composed of four major fractions (saturates, aromatics, resins, and asphaltenes) that differ from one another sufficiently in character such that identification can be achieved by application of relevant methods (Chapter 11). Indeed, although these four fractions are chemically complex, the methods of separation have undergone several modifications to such an extent that the evolution of the separation techniques is a study in itself (Chapter 10). In addition, because the fractions are in a balanced relationship in crude oil, the chemical character of these main fractions requires mention in this chapter.

Questions may also be raised regarding the usefulness of attempting to determine the exact structure of each complex material, such as asphaltenes, resins, and nonvolatile oils. Perhaps the answers lie not only in determining the locations of the heteroatoms (nitrogen, oxygen, and sulfur) but also in understanding the chemical reactions of the various constituents of petroleum. In fact, valuable data can be derived from chemical reactions; the process of understanding chemical reactions could result in a complementary evaluation of the structural types present in the hydrocarbon portions of these molecules in the hope of deriving as much benefit as possible during processing of these complex materials.

Whether these reasons are sufficiently valid remains to be seen, but considerable work has been done and is even now in progress to evaluate the influence of these *high-molecular-weight* materials during petroleum recovery and during petroleum refining (Speight, 1994; Yan et al., 1997).

The purpose of this chapter is to review a selection of methods that can be used for the identification of the chemical reactivity of petroleum constituents. Particular emphasis is placed on the techniques that have offered ready information and will continue to provide valuable information about the chemical constituents of petroleum. In this respect, in the past four decades, the reactions that cause the removal of the heteroatoms have been of particular interest.

Thus, this chapter presents methods that can be applied to study the makeup of the feedstock in terms of chemical structures as well as methods that might be preferred for refining. The chapter deals with the older methods that were used in the early days of structural group analysis; some of these are used even now. The evolution of the available spectroscopic techniques that could be applied to structural group analysis commenced in the 1960s (Chapter 11).

There is a range of chemical and thermal tests that can be applied to the analysis of petroleum, but the major focus of this chapter is on the actual chemistry of the various methods. Because the standard tests for such work are extremely limited, even nonexistent, it is necessary to rely on data from published works other than those of standards organizations. However, as a final series of thoughts in this

Introduction, the need for *control experiments* cannot be overstressed. Several experienced researchers have fallen foul of the lack of a control experiment that gives a basis for comparison. One might cite the deduction of asphaltenes structure using potassium naphthalide (a particularly vicious reagent) and asphaltenes. The researchers omitted to investigate the effect of this reagent on the solvent. Lo and behold, reaction occurred between the reagent and the solvent! Thus, the product mix became a very complex *mess of pottage* that should not have been used to draw any conclusions whatsoever (see Speight, 1994, for a discussion of this issue).

8.2. FUNCTIONAL GROUP ANALYSIS

The chemical analysis of the higher-boiling fractions of petroleum continues to be a challenge because of the wide variety of molecular types and structures present. Molecular types in the residua, heavy oil, and bitumen range from nonpolar, nonaromatic species to highly aromatic hydrocarbons, the molecular structures of which contain varying amounts of heteroatoms (nitrogen, oxygen, and sulfur) together with parts per million amounts of metals such as vanadium and nickel (Reynolds, 1998). The heteroatoms are often associated with polar, strongly interacting chemical functionality or functional groups that have a disproportionately large effect on the properties of each fraction and, therefore, on the whole feedstock (Speight, 1999, 2000 and references cited therein).

Because the number of molecules in residua, heavy oil, and bitumen with different chemical structures and reactivities is extremely large, determination of composition by separation of the feedstock into its molecular components is generally considered impractical if not impossible by many of the available techniques. However, if the different chemical functionalities (ASTM F-1186) that comprise the heavy feedstocks and therefore dominate their properties are considered, the number of types of functionalities that need to be considered decreases and becomes identifiable. Indeed, the heavy feedstocks can be safely assumed to contain these same functionalities, albeit in different proportions, depending on the origin and maturation conditions and the recovery and treatment of the feedstock (Speight, 1999). In turn, it is the interactions of these functions that can play a role in the structure of the feedstocks and their behavior under different conditions (Speight, 1999, 2000).

One of the principal agents in the behavior of heavy feedstocks is the various oxygen functions. These functions also play a major role in the structure of petroleum (Chapter 14). Thus identifying the presence (or the formation) of highly polar and strongly interacting chemical functional groups containing oxygen is a necessary step for assessing the effects of composition on properties and thus the performance of the feedstock during refining or the performance of asphalt in service.

During the past several decades, many studies have related to the identification and characterization of the polar, heteroatom-containing chemical functionality in various feedstocks. Infrared spectrometry has been a very prominent technique in this research because it can be applied to complex mixtures without alteration or destruction of the sample (Chapter 7).

Earlier researchers who explored infrared spectrometry (Chapter 7) for the characterization of the high-molecular-weight fraction of petroleum found the technique useful for determining the general chemical structural types present (Chapter 11). However, the strongly associating polar functionalities present often required extra and more conscientious effort. The inability to adequately characterize these polar functionalities resulted from inherent problems such as overlapping and ill-defined absorption bands and the shifting of absorption bands from hydrogen bonding.

These inherent problems have been overcome by the combined use of selective chemical reactions and differential spectrometry. A selective solvent system is also used to break up hydrogen bonding, eliminating the complicating effects of hydrogen bonding on the spectra (Moschopedis and Speight, 1976a).

In this section, the development and the current practice of the functional group analysis are presented and applications of the technique are described. The chemical functionalities quantitatively determined include carboxylic acids (and, independently, their salts), anhydrides, ketone oxygen, 2-quinolone-type oxygen, sulfoxide oxygen, pyrrole-type nitrogen, and phenolic oxygen. With the exception of basic nitrogen compounds (predominantly pyridine-type nitrogen), which do not yield readily to infrared analysis, these functionalities make up the important polar heteroatom-containing functionalities present (to different extents) in feedstocks.

As mentioned above, the most polar and strongly interacting functional groups in residua, heavy oil, and bitumen occur in relatively small amounts and their infrared absorption bands are often complicated by hydrogen bonding and overlap with other strong absorption bands (Moschopedis and Speight, 1976a), making their detection difficult and their quantitative assessment virtually impossible without the use of special techniques.

Phenolic and pyrrolic groups in heavy feedstock are hydrogen-bonding functionalities. Thus, in solutions of these feedstocks in typical infrared spectral solvents, an equilibrium exists between the free absorption bands of these functional groups and their hydrogen-bonding bands (the latter bands overlap); this equilibrium is dependent on the concentration, the solvent characteristics, and the basic character of the constituents in the feedstock with which the acidic hydrogen of the functionalities interacts (Moschopedis and Speight, 1976a).

Two other important naturally occurring functionalities are carboxylic acids and 2-quinolone-type oxygen. These functionalities are extremely strong hydrogen bonders. Not only do they readily form dimers but they also interact strongly with

each other to form a mixed dimer, yielding six absorption bands, of which five overlap and become virtually indistinguishable. However, it must be remembered that sample history can play a major role in the occurrence of such functions in the feedstock. Oxidation during heavy oil recovery can, and does, cause oxygen incorporation into the feedstock, and the occurrence of carboxylic acid function in residua and heavy oil may be diminished by the thermal treatment (even distillation) used to produce the heavy feedstock. The incorporation of oxygen functions can have a noticeable influence on the inter- and intramolecular bonding arrangements in the feedstock (Moschopedis and Speight, 1976b).

To overcome the problems just described and to obtain spectra suitable for quantitative analysis, several specialized techniques and procedures have been employed. Tetrahydrofuran (THF) solvent has been used to eliminate interference from hydrogen bonding on the carbonyl absorption region in the determination of ketones, carboxylic acids, anhydrides, and 2-quinolones. However, caution is advised because this solvent is not always capable of dissolving the asphaltene constituents and may lead to faulty conclusions because of the occurrence of suspended organic matter.

Whatever solvent is used, advantage can be taken of the hydrogen bonding of phenolic and pyrrolic functionality in the analysis of these functional groups. However, because the solvent employed may have absorption bands in the frequency ranges used in the determinations, a solvent compensation technique must be used.

Thus, when the problem of hydrogen bonding has been eliminated, the problem of overlapping bands in the carbonyl absorption region (about 1800 cm^{-1} to about 1600 cm^{-1}) is addressed by using selective chemical reactions and differential infrared spectrometry. The techniques applied are as follows. To reveal the absorption band of interest and to eliminate from the spectra other bands with absorption at the same frequency, the sample is treated with a selective reagent that eliminates or shifts the absorption band of interest to another frequency.

A differential spectrum is then taken with the treated sample in one beam and the untreated sample in the other beam of a double-beam infrared spectrophotometer. This procedure reveals the absorption band of the functionality of interest in the differential spectrum and nulls or cancels out all other absorption bands in the same region. Quantitative analysis can also be applied to the absorption band of interest using calculations of the areas under the absorption bands.

The apparent integrated absorption intensity (B), in units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-2}$, of an infrared absorption band obtained on a spectrophotometer having a monochromatic energy source and finite slit width is defined as follows:

$$B = -1/cI \ln(T_0/T)_v d\nu$$

where c is the concentration of functional group type (mol L^{-1}), l is the cell path length (cm), ν is the absorption frequency (cm^{-1}), T_0 is the incident radiation, and T is the transmitted radiation.

The area under the absorbance versus absorption-frequency curve for the absorption bands of interest is represented by the term $\ln(T_0/T)_\nu d\nu$. The term $\ln(T_0/T)$ is equivalent to the commonly used term *absorbance*, designated by the notation A .

The band area, $A_\nu d\nu$ can be estimated by counting squares on the recording chart paper or by weighing the paper, which represents the respective peak areas. The concentrations of functional group types in the sample are then estimated by using the equation

$$c = \Delta A_\nu d\nu / Bl \times 1.05 / 0 / 0.05$$

The potential applications of the functional group analysis in composition-related technology are numerous. Thus the combined use of differential infrared spectrometry and selective chemical reactions provided the basis for the development of an analytical method for the quantitative analysis of important chemical functionality in feedstocks. The method can be applied to the solution of a variety of composition-related problems in petroleum technology.

Another form of functional group analysis involves measurement of the acidity of a sample.

The total *acidity* (usually referred to as the *acid number*) is the quantity of base, expressed in milligrams of potassium hydroxide, required to neutralize the acidic constituents in 1 g of sample under the conditions of the test (ASTM D-664, IP 1, IP 37, IP 139, IP 177, IP 182, IP 213, IP 354, IP D-431). Acidity generally increases with viscosity for heavy oil and bitumen, but no reason for this correlation has been established.

Severely weathered bitumen, such as that found in outcrops, is more acidic than unoxidized bitumen from deeper within the deposit. In addition, correlations have been established between the acid number of heavy oils produced in a fireflood and the location of the fire front. An increase in the acid number of petroleum and heavy oil can lead to increasing emulsion stability and therefore emulsion-treating difficulties after recovery operations.

One method (ASTM D-664) involves dissolution of the sample in a toluene-water-isopropanol (50.0:0.5:49.5) solution titrated potentiometrically with 0.1 N alcoholic potassium (KOH) using a glass indicating electrode and a calomel reference electrode. The end point is determined either graphically or, if no inflections in the curve are apparent, by titration to a meter reading for a standard buffer solution.

Another standard method (IP 213) involves the determination of the neutralization value of asphalt (bitumen) using a potassium hydroxide solution (0.1 N in distilled water), standardized by potentiometric titration with potassium hydrogen

phthalate. The sample to be titrated may be dissolved in a toluene-ethanol-water solution. Excess base is added, and the mixture is backtitrated with 0.1 N standardized hydrochloric acid to an alkali blue end point.

A modification of this method (ASTM D-6441) uses the solvent systems and reagents as specified (IP 213) but with a direct potentiometric titration using 0.1 N aqueous potassium. A titroprocessor in combination with a lithium chloride (LiCl) electrode gives the sensitivity required to identify the end point by inflection.

Two other methods (ASTM D-974 and ASTM D-3339, IP 139) also involve colorimetric titration to determine the acid number of petroleum products and lubricants by titration with 0.1 N potassium hydroxide in a toluene-isopropyl alcohol mixture to a *p*-naphtholbenzein indicator end point. The application for titration of heavy oil and bitumen is hampered because of the difficulty in detecting the color change from orange to green-brown. A potentiometric perchloric acid titration method (ASTM D-2896) is also available for the determination of acid number.

In addition, application of any of the methods to heavy oil and bitumen (or even to whole crude oil) can be influenced by precipitation of asphaltenes on the electrodes during a potentiometric titration. This effect can delay the response of the electrode. When the precipitation problem is severe, inflections in the titration curve cannot be identified and titration to a buffer end point becomes slow and imprecise.

Indeed, determination of the acid number of heavy oil and bitumen is subject to uncertainties due to the problem of precipitation of components during titration. Reduction of test sample size, use of alternate solvent systems, and minimization of titration time, possibly by using a more concentrated titrant, may improve precision. These factors should be examined to establish a method suitable for these heavy feedstocks.

There is also a method for the determination of the basic constituents in petroleum products (ASTM D-4739). The data are presented as a *base number*, which is defined as the quantity of acid, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point (IP 139, IP 276, IP 400, IP 417).

The base number can be used to indicate the relative changes that occur in petroleum or a petroleum product during use (or storage) under service (or oxidizing) conditions regardless of color or other properties of the resulting product.

The *neutralization value* either by potentiometric titration (ASTM D-664) or by color-indicator titration (ASTM D-974) provides base numbers as well as acid numbers. Further functionality can be determined by use of *saponification numbers* using the color-indicator titration method (ASTM D-94) or the potentiometric titration method (ASTM D-939, IP 2).

The *bromine number* (ASTM D-1159, IP 129, IP 130) is the number of grams of bromine consumed by a weighed amount (100 g) of sample when reacted under specified conditions (ASTM D-1159). In theory, the method gives an indication of

the amount of unsaturation in the sample by assuming that additions of bromine across multiple carbon-carbon bonds are the only reactions. However, with the heavier feedstocks, caution is needed in the interpretation of the data because of the ready reactivity of bitumen constituents with bromine (Moschopedis and Speight, 1971).

The ASTM method uses a polarized electrode pair. As soon as there is a small amount of excess bromine, the solution conductivity increases sharply, producing a large, clearly defined deflection at the end point.

In this method, the sample is initially dissolved in a solvent consisting of glacial acetic acid, 1,1,1-trichloroethane, methanol, and sulfuric acid. The solution is titrated with bromide-bromate titrant using dual platinum electrodes and a 10- μ A polarizing current for end-point detection.

Alternatively, the *bromine index* is the number of milligrams of bromine that will react with 100 g of the sample (IP 299). This index is used mostly by the chemical industry for stocks that have an unusually low olefin content.

8.3. HYDROGENATION

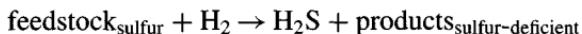
The purpose of hydrogenating petroleum constituents is (1) to improve existing petroleum products or develop new products or even new uses, (2) to convert inferior or low-grade materials into valuable products, and (3) to transform higher-molecular-weight constituents into liquid fuels. Indeed, it is generally recognized that the higher the hydrogen content of a petroleum product, especially the fuel products, the better the quality of the product. This knowledge has stimulated the use of hydrogen-adding processes in the refinery.

However, in the context of this chapter, i.e., in the chemical laboratory, the hydrogenation of petroleum and the heavy feedstocks (heavy oil, bitumen, and residua) is somewhat limited by the nature or requirements of the reaction conditions. For example, high temperatures and pressures are usually required, which cause changes to the hydrocarbon skeleton. However there are mild hydrogenating processes that can be applied to petroleum, thereby providing information about the constituents. In fact, the focus of hydrogenation in the laboratory tends to be oriented toward the category often referred to as nondestructive or mild hydrogenation.

The hydrogenation of petroleum has been studied extensively for the past several decades and to repeat much of the work here would be superfluous. Thus it is the intent here to discuss only the basic principles of hydrogenation and to point out the methods that might be used to analyze the products. Such a discussion is more in keeping with the nature of this book.

The basic chemical concept of the hydrogenation process as applied to petroleum is to convert the organic constituents to liquid fuels and, at the same time, to

remove the organic heteroatoms in the feedstock by conversion to their hydrogen analogs.



It is the chemical aspects of this reaction that can be most important as a means of building the basis for refining.

As an example of the laboratory hydrogenation reaction, reduction by Raney nickel is a mild degradation method. It may be performed, for example, by reacting a 10-mg sample with a suspension of 0.5 mg of catalyst in 2.5 ml of refluxing absolute alcohol for 1–2 h under nitrogen but may require that the sample is molecularly dissolved. However, there may be drawbacks to the use of such a method, because solubility of the constituents in the solvent is often necessary. In addition, the fact that asphaltene constituents form aggregates (Chapter 12) may cause interference with the method and provide data that are, at best, questionable.

Asphaltenes may also be hydrogenated to produce resins and oils at elevated temperatures ($>250^{\circ}\text{C}$) (Speight, 1999, 2000, and references cited therein). Chemical hydrogenation under much milder conditions, for example with lithium-ethylenediamine or sodium-liquid ammonia, also produces lower-molecular-weight species together with marked reductions in the sulfur and oxygen contents.

In a more general chemical sense, the effect of hydrogen on naphthenic hydrocarbons is mainly that of ring scission followed by immediate saturation of each end of the fragment produced. The ring is preferentially broken at favored positions, although generally all the carbon-carbon bond positions are attacked to some extent.

Aromatic hydrocarbons are resistant to hydrogenation under mild conditions, but, under more severe conditions the main reactions are conversion of the aromatic to naphthenic rings and scissions within the alkyl side chains. The naphthenes may also be converted to paraffins. Polynuclear aromatic hydrocarbons are more readily attacked than the single-ring compounds, the reaction proceeding by a stepwise process in which one ring at a time is saturated and then opened.

Starting in the 1950s, there was considerable focus on hydrogenation as a means of sulfur removal from crude oil; this will be the focus of the present discussion because it illustrates many of the aspects of the hydrogenation of petroleum, heavy oil, and bitumen.

Thus the thermodynamics of the hydrogenation reaction can be evaluated from the equilibrium constants of typical desulfurization or partial desulfurization reactions such as

1. hydrogenation of model compounds to yield saturated hydrocarbons ($R-H$) and hydrogen sulfide (H_2S),
2. decomposition of model compounds to yield unsaturated hydrocarbons ($R-CH=CH-R^1$) and hydrogen sulfide (H_2S),
3. decomposition of alkyl sulfides to yield thiols ($R-SH$) and olefins ($R-CH=CH-R^1$),
4. condensation of thiols ($R-SH$) to yield alkyl sulfides ($R-S-R^1$) and hydrogen sulfide (H_2S), and
5. hydrogenation of disulfides ($R-S.S-R^1$) to yield thiols ($R-SH$, R^1-SH).

The logarithms of the equilibrium constants for the reduction of sulfur compounds to saturated hydrocarbons over a wide temperature range (Speight, 2000) are almost all positive, indicating that the reaction can virtually proceed to completion if hydrogen is present in the stoichiometric quantity. The equilibrium constant does, however, decrease with increasing temperature for each particular reaction but still retains a substantially positive value at 425°C (795°F), which is approaching the maximum temperature at which many of the hydrodesulfurization (especially nondestructive) reactions would be attempted. The data also indicate that the decomposition of sulfur compounds to yield unsaturated hydrocarbons and hydrogen sulfide is not thermodynamically favored at temperatures below 325°C (615°F), and such a reaction has no guarantee of completion until temperatures of about 625°C (1,155°F) are reached. However, substantial decomposition of thiols can occur at temperatures below 300°C (570°F); in fact (with only few exceptions), the decomposition of all saturated sulfur compounds is thermodynamically favored at temperatures below 425°C (795 °F).

Kinetic studies using individual compounds, especially for the hydrodesulfurization reaction, have usually indicated that first-order kinetics with respect to sulfur is the predominant mechanism by which sulfur is removed as hydrogen sulfide.

The structural differences between the various sulfur-containing molecules make it impractical to have a single rate expression applicable to all reactions in hydrodesulfurization. Each sulfur-containing molecule has its own hydrogenolysis kinetics, which is usually complex because several successive equilibrium stages are involved and these are often controlled by internal diffusion limitations during refining.

Thiophenic compounds are the most refractory of the sulfur compounds. Consequently, thiophene is frequently chosen as representative of the sulfur compounds in feedstocks (Speight, 1999, 2000). The hydrogenolysis of thiophene takes place according to two distinct paths. The first path leads through thiophane to butylmercaptan in equilibrium with butene and dibutylthioether and finally to butene and hydrogen sulfide. It is considered unlikely that the thiophene and the dibutylsulfide

can undergo direct hydrogenolysis with production of hydrogen sulfide. However, it is possible that the butyl mercaptan can be decomposed according to the two parallel paths, namely

1. desulfurization of the mercaptan on the active metal sulfides and acid sites of alumina followed by hydrogenation of the intermediate butene, and
2. direct hydrogenolysis of the C—SH bond on the active metal sulfides.

As complex as the desulfurization of thiophene might appear, projection of the kinetic picture to benzothiophene and dibenzothiophene, and to their derivatives, is even more complex. However, kinetic data derived from model compounds cannot be expected to include contributions from the various steric effects, which are a consequence of complex molecules containing three-dimensional structures (Isoda et al., 1996a,b).

Furthermore, the complexity of the individual reactions occurring in an extremely complex mixture and the *interference* of the products with those from other components of the mixture is unpredictable. Or the interference of secondary and tertiary products with the course of a reaction and, hence, with the formation of primary products may also be cause for concern. Hence, caution is advised when applying the data from model compound studies to the behavior of petroleum, especially the molecularly complex heavy oils. These have few, if any, parallels in organic chemistry. In addition, all such contributions may be missing from the kinetic data, which must be treated with some degree of caution.

However, there are several generalizations that come from the available thermodynamic data and investigations of pure compounds as well as work carried out on petroleum fractions (Gray, 1994, and references cited therein). Thus, at room temperature, hydrogenation of sulfur compounds to hydrogen sulfide is thermodynamically favorable, and the reaction will essentially proceed to completion in the presence of a stoichiometric amount of hydrogen. Sulfides, simple thiophenes, and benzothiophenes are generally easier to desulfurize than the dibenzothiophenes and the higher-molecular-weight condensed thiophenes.

Nevertheless, the development of general kinetic data for the hydrogenation of different feedstocks is complicated by the presence of a large number of compounds, each of which may react at a different rate because of structural differences as well as differences in molecular weight and may be reflected in the appearance of a complicated kinetic picture in which the kinetics is not, apparently, first order (Scott and Bridge, 1971). The overall reaction may be satisfied by a second-order kinetic expression when it can, in fact, also be considered as two competing first-order reactions.

Thus it has become possible to define certain general trends that occur in the hydrogenation of petroleum feedstocks. One of the more noticeable facets of the process is that the rate of reaction declines markedly with the molecular weight

of the feedstock (Scott and Bridge, 1971). It should be noted here that, because of the nature of the reaction, steric influences would be anticipated to play a lesser role in the hydrocracking process.

Residua hydrogenation is considerably more complex than the hydrodesulfurization of model organic sulfur compounds or, for that matter, narrow-boiling petroleum fractions. In published studies of the kinetics of residua hydrogenation, one of three approaches has generally been taken:

1. The reactions can be described in terms of simple first-order expressions.
2. The reactions can be described by use of two simultaneous first-order expressions, one expression for easy-to-hydrogenate systems and a separate expression for difficult-to-hydrogenate systems, with special reference to the removed sulfur.
3. The reactions can be described using a pseudo-second-order treatment.

Each of the three approaches has been used to describe hydrogenation of residua under a variety of conditions with varying degrees of success, but it does appear that pseudo-second-order kinetics are favored. In this particular treatment, the rate of hydrogenation (hydrodesulfurization) is expressed by a simple second-order equation:

$$C/1 - C = k(1/\text{LHSV})$$

where C is the wt% sulfur in product/wt% sulfur in the charge, k is the reaction rate constant, and LHSV is the liquid hourly space velocity (volume of liquid feed per hour per volume of catalyst). Application of this model to a residuum desulfurization gave a linear relationship (Beuther and Schmid, 1963; Ozaki et al., 1963).

On this basis, the use of two simultaneous first-order equations may be more appropriate. The complexity of the constituents tends to increase with an increase in boiling point, and the reactivity tends to decrease with complexity. It is anticipated that such an approach is consistent with the relative reactivity of various compound types observed for model compounds and for the various petroleum fractions that have been investigated.

Other kinetic work has shown that, for a fixed level of sulfur removal, the order of a reaction at constant temperature can be defined with respect to pressure:

$$k = 1/\text{LHSV}(P_h)^n$$

where P_h is the hydrogen partial pressure, LHSV is the liquid volume hourly space velocity, k is a constant, and n is the order of the reaction. It has been concluded, on the basis of this equation, that the hydrodesulfurization of residuum is first-order

with respect to pressure over the range 800–2,300 psi, although it does appear that the response to pressure diminishes markedly (and may even be minimal) above 1,000 psi.

Despite all of the work, the kinetics and mechanism of alkyl-substituted dibenzothiophene, in which the sulfur atom may be sterically hindered, are not well understood and these compounds are in general very refractory to hydrodesulfurization. Other factors that influence the desulfurization process such as catalyst inhibition or deactivation by hydrogen sulfide, the effect of nitrogen compounds, and the effect of various solvents must be studied to obtain a comprehensive model that is independent of the type of model compound or feedstock used.

Throughout this section, the focus has been on the kinetic behavior of various organic molecules during refinery operations and specifically during the hydrodesulfurization process. However, it must be remembered that the kinetic properties of the catalyst also deteriorate because of deposits on its surface. Such deposits typically consist of coke and metals that are products of the various chemical reactions.

During hydrogenation at higher temperatures, essentially all the initial reactions of catalytic cracking occur, but some of the secondary reactions are inhibited or stopped by the presence of hydrogen. For example, the yields of olefins and the secondary reactions that result from the presence of these materials are substantially diminished and branched-chain paraffins undergo demethanation. The methyl groups attached to secondary carbons are more easily removed than those attached to tertiary carbon atoms, whereas methyl groups attached to quaternary carbons are the most resistant to hydrocracking.

On an individual hydrocarbon type basis, and without the effects of hydrodesulfurization, the effect of hydrogen on naphthenic hydrocarbons is mainly that of ring scission followed by immediate saturation of each end of the fragment produced. The ring is preferentially broken at favored positions, although generally all the carbon-carbon bond positions are attacked to some extent. For example, methylcyclopentane is converted (over a platinum-carbon catalyst) to 2-methylpentane, 3-methylpentane, and *n*-hexane.

Aromatic hydrocarbons are resistant to hydrogenation under mild conditions, but, under more severe conditions, the main reactions are conversion of the aromatic to naphthenic rings and scissions within the alkyl side chains. The naphthenes may also be converted to paraffins.

Polynuclear aromatics are more readily attacked than the single-ring compounds, the reaction proceeding by a stepwise process in which one ring at a time is saturated and then opened.

One might wonder where analytical chemistry fits into all of this. Once the hydrogenation reaction has been carried out, it is then the focus of the chemist or analytical chemist to determine the reaction pathway using the various analyses that can be brought to bear on the issue.

First, there is the analysis of gaseous product such as hydrogen sulfide (ASTM D-103, ASTM D-2385, ASTM D-2725, ASTM D-4084, ASTM D-4810, IP 401) or the composition of the gas as might be applied to the analysis of natural gas (ASTM D-1945, ASTM D-2597, IP 345) and the composition of the liquid in terms of hydrocarbon types (IP 156). With respect to liquid products, gas chromatographic analysis (Chapter 10) and high-performance liquid chromatographic analysis (Chapter 10) of the organic liquid products might be the first techniques to be applied. Simulated distillation (Chapter 10) as well as the determination of compound class types by adsorption chromatography (Chapter 10) would also be beneficial. This might be followed by elemental analysis of the individual fractions as well as by infrared spectroscopy (Chapter 7) and mass spectrometry (Chapter 7) with the potential for application of nuclear magnetic resonance spectroscopy being very real.

8.4. OXIDATION

The oxidation of petroleum and its fractions has, like hydrogenation, been the object of study for several decades with the focus being predominantly on the chemistry of asphalt oxidation. Because asphalts have high proportions of asphaltenes, it is not surprising that the oxidation of asphaltenes has been studied widely, not only from the perspective of asphalt production but also from the perspective of structural studies.

However, for the most part, the oxidation of petroleum fractions will be dealt with elsewhere, especially as to how oxidation relates to instability and incompatibility (Chapter 13).

Oxidation of asphaltenes with common oxidizing agents, such as acid and alkaline peroxide, acid dichromate, and alkaline permanganate, is a slow process. The occurrence of a broad band centered at 3420 cm^{-1} and a band at 1710 cm^{-1} in the infrared spectra of the products indicates the formation of phenolic and carboxyl groups during the oxidation. Elemental analyses of the products indicate that there are two predominant oxidation routes, notably

1. the oxidation of naphthalene moieties to aromatics as well as the oxidation of *active* methylene groups to ketones, and
2. severe oxidation of naphthalene and aromatic functions, resulting in degradation of these systems to carboxylic acid functions.

Oxidation of asphaltenes in solution by air and in either the presence or absence of a metal salt is also possible (Moschopedis and Speight, 1978). There is some oxygen uptake, as can be seen from the increased O-to-C atomic ratios, but the most obvious effect is the increase in the amount of *n*-heptane-insoluble material.

In addition, analyses of the data show that it is the higher heteroatoms (more polar constituents) of the asphaltenes that are more susceptible to oxidation, suggesting that the polarity of the constituents may be determined by the incorporation of the heteroatoms into ring systems.

Air blowing of asphaltenes at various temperatures brings about significant oxygen uptake. This is accompanied by a marked decrease in the molecular weight (vapor pressure osmometry, benzene solution) of the product. This indicates that intermolecular hydrogen bonding of oxygen functionality may play a part in the observed high molecular weights and physical structure of petroleum (Moschopedis and Speight, 1978; see also Taft et al., 1996).

It may appear, at first sight, that sulfur and oxygen exist as linkages among hydrocarbon segments of asphaltene molecules. Although this may be true, in part, it is also very likely, in view of what has been discussed previously, that the lower molecular weights reflect changes in molecular association brought about by the elimination of oxygen and sulfur.

Aromatics undergo *condensation with formaldehyde* to afford a variety of products. This process can be extended to the introduction of various functions into the asphaltene molecules, such as *sulfomethylation*, that is, introduction of the $-\text{CH}_2\text{SO}_3\text{H}$ group. This latter process, however, usually proceeds more readily if functional groups are present within the asphaltene molecule.

Thus oxidation of asphaltenes produces the necessary functional groups, and subsequently sulfomethylation can be conveniently achieved. The occurrence of sulfomethylation of the oxidized asphaltenes can be confirmed from three sources:

1. overall increases in the sulfur contents of the products relative to those of the starting material,
2. the appearance of a new infrared absorption band at 1030 cm^{-1} attributable to the presence of sulfonic acid group(s) in the molecule(s), and
3. the water solubility of the products, a characteristic of this type of material.

These sulfomethylated oxidized asphaltenes remain in solution even after parent oxidized asphaltenes can be precipitated from alkaline solution by acidification to pH 6.5.

The facile sulfomethylation reaction indicates the presence in the starting materials of reactive sites *ortho* or *para* to a phenolic hydroxyl group. The related reaction, sulfonation, is also a feasible process for oxidized asphaltenes. The ease with which this reaction proceeds suggests the presence of quinoid structures in the oxidized materials. Alternatively, active methylene groups in the starting materials facilitate sulfonation, because such groups have been known to remain intact after prolonged oxidation.

The *chemical reactions* of the resins have received much less attention than the reactions of the asphaltenes, and usually only fragmentary reports are available. Like the chemical reactions of the asphaltene constituents, the chemical reactions

of the resin constituents give indications of the structural types within these constituents. The reactions also indicate the effects that changes in the hydrocarbon structure or functionality will have on the properties of the resin constituents (see Speight, 1991, for more detail).

One area of resin chemistry that has received attention is the interaction with oxygen. Thus the *oxidation* of resins in benzene solution with air in the presence or absence of various metal salts proceeds readily to yield asphaltene products (Moschopedis and Speight, 1978). Substantial uptake of oxygen occurs, and, from the atomic heteroatom-to-carbon ratios in the starting material and products, it appears that preferential reaction of the more polar entities occurs. Resins also undergo *condensation with formaldehyde*, which is especially rapid after the introduction of oxygen functions by oxidation. Resins can also be *sulfonated* to yield water-soluble or oil-soluble sulfonates. Resins react with *nitric acid* to yield complex mixtures of oxidation and nitration products. Reactions with *sulfur* cause dehydrogenation as well as the formation of complex sulfides. The overall result is the production of higher-molecular-weight material with low hydrogen content.

Resins also react with *diazocompounds*, which not only produces asphaltene-type products but also can be used to introduce various functional groups into the molecule. Resins react with *acetic anhydride* to afford a variety of acetylated products.

Just as the asphaltenes and resins react with oxygen at low temperatures ($<100^{\circ}\text{C}$, $<212^{\circ}\text{F}$), so do the oils. Thus *oxidation* in benzene solution by air, in either the presence or absence of metal salts, proceeds smoothly to yield asphaltene and resin products (Moschopedis and Speight, 1978). In general, the majority of the oil recovered after oxidation has lower atomic N-to-C and S-to-C ratios than the untreated oil; this indicates that it is the more polar components of the oil fraction that are susceptible to oxidation. It is also evident that the presence of catalytic amounts of metal salts causes an acceleration in the oxidation rate of the oil fraction.

Selective oxidation with sodium periodate (NaIO_4) catalyzed by ruthenium ions (Ru^{8+}), can give more specific information on the nature of asphaltene constituents. This method selectively oxidizes alkyl-substituted aromatic carbons to carbon dioxide, leaving behind (1) alkyl substituents as monocarboxylic acids, and (2) polymethylene bridges between aromatic rings as α,ω -dicarboxylic acids. Some of the condensed aromatic rings survive the treatment as benzene polycarboxylic acids. The various acids are made volatile by esterification with diazomethane, and the esters can be analyzed by gas chromatography-mass spectrometry (Mojelsky et al., 1992).

This technique provides the distribution of alkyl substituents attached to aromatic rings, that of paraffin chains connecting two aromatic rings or ring systems, and information on the nature of the aromatic and naphthenic ring systems in the original sample. The amounts of alkyl chains found this way seem to be reasonably

quantitative. Those of aromatic and naphthenic rings appear more tentative because the fate of the aromatic heterocompounds is not known except that some of the sulfur compounds are recovered in the form of sulfones.

Oxidation is also used for the separation of neutral sulfur compounds from hydrocarbons (see, e.g., Drushel, 1972; Ruiz et al., 1982; Arpino et al., 1987). The sulfur compounds are converted to sulfoxides and sulfones that are strongly retained on chromatographic columns and can thus be separated from the hydrocarbons. After recovery, they can be reconverted to the sulfides by reduction with lithium aluminum hydride (LiAlH_4) for further analysis. By combining such oxidation and reduction procedures, it was possible to distinguish between thiophene derivatives and three different types of sulfides.

The issue, of course, with any chemical procedure is the occurrence of side reactions that may occur, especially in such oxidative procedures.

Again, with the results of hydrogenation experiments, one might wonder where analytical chemistry fits into all of this. Once the oxidation reaction has been carried to completion or to the desired point, it is then the focus of the chemist or analytical chemist to determine the reaction pathway using the various analyses that can be brought to bear on the issue.

For example, gas chromatographic analysis (Chapter 10) and high-performance liquid chromatographic analysis (Chapter 10) of the organic liquid products might be the first techniques to be applied. Simulated distillation (Chapter 10) as well as the determination of compound class types by adsorption chromatography (Chapter 10) would also be beneficial. This might be followed by elemental analysis (Chapter 4) of the individual fractions as well as by infrared spectroscopy (Chapter 7) and mass spectrometry (Chapter 7), with the potential for application of nuclear magnetic resonance spectroscopy (Chapter 7) being very real.

8.5. HALOGENATION

Halogenation of petroleum and its fractions occurs readily to afford the corresponding halo-derivatives; the physical properties of the halogenated materials are markedly different from those of the parent materials. Analysis for the various halogens is possible (ASTM E-422).

In the case of the asphaltenes, which again have been the recent focal point of the investigations, for example, the unreacted asphaltenes are dark brown, amorphous, and readily soluble in benzene, nitrobenzene, and carbon tetrachloride, but the products are black, shiny, and only sparingly soluble, if at all, in these solvents.

There are also several features that distinguish the individual halogen reactions from one another. For example, during *chlorination* of asphaltenes, there is a cessation of chlorine uptake by the asphaltenes after 4 h. Analytical data indicate

that more than 37% of the total chlorine in the final product is introduced during the first 0.5 h, reaching the maximum after 4 h. Furthermore, the H-to-C ratio of 1.22 in the parent asphaltenes [(H + Cl)-to-C ratio in the chlorinated materials] remains constant during the first 2 h of chlorination, by which time chlorination is 88% complete. This is interpreted as substitution of hydrogen atoms by chlorine in the alkyl moieties of the asphaltenes; the condensed aromatic sheets remain unaltered because substitution of aryl hydrogen appears to occur readily only in the presence of a suitable catalyst, such as ferric chloride (FeCl_3), or at elevated temperatures. It is only after more or less complete reaction of the alkyl chains that addition to the aromatic rings occurs, as evidenced by the increased atomic (H + Cl)-to-C ratios in the final stages of chlorination.

Bromine uptake by the asphaltenes is also complete in a comparatively short time (<8 h). However, in contrast to the chlorinated products, the atomic (H + halogen)-to-C ratio remains fairly constant (1.23 and 1.21 in the bromoasphaltenes or 1.22 in the unreacted asphaltenes) over the prolonged periods (up to 24 h) of the bromination.

Iodination of asphaltenes is different insofar as a considerable portion of the iodine, recorded initially as iodine uptake, can be removed by extraction with ether or with ethanol, whereas very little weight loss is recorded after prolonged exposure of the material to a high vacuum. The net result is the formation of a product with an atomic (H + I)-to-C ratio of 1.24 after an 8-h reaction; a more prolonged reaction period affords a product with a (H + I)-to-C ratio of 1.17. This latter finding may be the result of iodination of the alkyl or naphthenic moieties of the asphaltenes with subsequent elimination of hydrogen iodide. Alternatively, dehydrogenation of naphthene rings to aromatic systems or coupling of aromatic nuclei would also account for lower (H + I)-to-C ratios. In fact, this latter phenomenon could account, in part, for the insolubility of the products in solvents that are normally excellent for dissolving the unchanged asphaltenes. However, it will be appreciated that these aforementioned reactions are only a few of the many possible reactions that can occur, and undoubtedly halogenation of the asphaltenes is much more complex than would appear from the product data.

The *iodine value* of various oils and their derivatives (ASTM D-1541, ASTM D-1959, IP 84) can be measured, thereby giving data that will complement the bromine number. Halogenation of the asphaltenes can also be achieved with the use of sulfonyl chloride, iodine monochloride, and *N*-bromosuccinimide or indirectly via the Gomberg reaction. As an addition to this segment, it is worthwhile to note that iodine monochloride is used as the chemical means for detecting lead in gasoline (ASTM D-3341, IP 270).

Halogens react with the oils relatively slowly, especially if there is no olefinic ($>\text{C}=\text{C}<$) or aromatic unsaturation; essentially, substitution reactions occur. At elevated temperatures, dehydrohalogenation occurs, giving rise to resin and asphaltene products.

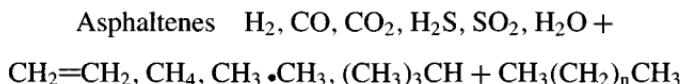
8.6. THERMAL METHODS

The simplest thermal methods of analysis of petroleum, heavy oil, bitumen, residua, and their respective fractions are, of course, the carbon residue tests (Chapter 5).

Briefly, and by way of introduction to this section, the carbon residue of crude oil and crude oil products is a measure of the propensity of the sample to form coke when combusted under specific conditions that require a limited supply of oxygen. The carbon residue of a petroleum sample might be considered to be analogous to the determination of fixed carbon for coal (ASTM D-3172, ASTM D-3173, ASTM D-3174, ASTM D-3175).

There is a range of other thermal tests that can also be applied (Chapter 5), but the major focus of this section is on the actual chemistry of the thermal decomposition process. Because the standard tests for such work are extremely limited, even nonexistent, it is necessary to rely on data from published works other than those of standards organizations.

Asphaltenes can be *thermally decomposed* under conditions similar to those employed for visbreaking (viscosity breaking; around 470°C, 880°F) to afford, on the one hand, light oils that contain higher (to at least C₃₆) paraffins and, on the other hand, coke:



The thermal decomposition of asphaltenes provides an excellent example of inconsistencies in the derivation of structural types from spectroscopic materials (i.e., magnetic resonance) in which alkyl side chains are deduced to contain approximately four carbon atoms (Speight, 1970, 1971). Asphaltene pyrolysis (350–800°C, 660–1470°F) produces substantial amounts of alkanes (having up to 40 carbon atoms in the molecule) in the distillate, which can only be presumed to reflect the presence of such chains in the original asphaltene. Transalkylation studies (Farcasiu et al., 1983) also provide evidence for longer alkyl chains. Obviously, recognition of the inconsistencies of the spectroscopic method with respect to the paraffinic moieties must lead to the recognition of similar inconsistencies when considering the aromatic nucleus.

The application of thermal techniques to study the nature of the volatile thermal fragments from petroleum asphaltenes has produced some interesting data relating to the polynuclear aromatic systems (Speight, 1971; Ritchie et al., 1979; Schucker and Keweshan, 1980; Gallegos, 1981; Paul, 1982). These thermal techniques have produced strong evidence for the presence of small (1- to 4-ring) polynuclear aromatic systems (Speight and Pancirov, 1984), and, now, application

of the technique to the various functional fractions has confirmed the general but unequal distribution of these systems throughout asphaltenes.

Each asphaltene fraction produced the same type of polynuclear aromatic systems (Moschopedis and Speight, 1978) in the volatile matter, but the distribution was not constant. It was also possible to compute the hydrocarbon distribution; a noteworthy point here is the overall preponderance of single-ring (cycloparaffin and alkylbenzene) species as well as the domination of saturated material over aromatic material. The preponderance of the low-molecular-weight material in the volatile products is anticipated on the basis that more complex systems remain as nonvolatile material and, in fact, are converted to coke. One other noteworthy point is that the pyrolysis-gas chromatography-mass spectrometry (py/gc/ms) program does not accommodate nitrogen and oxygen species. This matter is resolved, in part, by the concentration of nitrogen and oxygen in the nonvolatile material (coke) and the overall low proportions of these heteroatoms originally present in the asphaltenes.

The major drawback to the application of a py/gc/ms technique to the study of the polynuclear aromatic systems in petroleum asphaltenes is the amount of material that remains as a nonvolatile residue. Aside from speculation about the polynuclear aromatic systems in the residue, it should be noted that the majority of the nitrogen (>90%), oxygen (>50%), and sulfur (>60%) in the natural asphaltene remains in the coke (Speight, 1971; Speight and Pancirov, 1984).

Paraffins are not the only hydrocarbon products of the thermal reactions of asphaltenes. The reaction paths are extremely complex; spectroscopic investigations indicate an overall dealkylation of the aromatics to methyl (predominantly) or ethyl (minority) groups. This is in keeping with a mass spectroscopic examination of asphaltene fractions (by direct introduction into the ionization chamber), which indicates a progressive increase with increasing temperature (50–350°C, 120–660°F) of ions attributable to low-molecular-weight hydrocarbons. Higher temperatures (500°C, 932°F) promote the formation of benzene and naphthalene nuclei as the predominant aromatics in the light oil, but unfortunately an increase in coke production is noted.

In conclusion, thermal decomposition of asphaltenes affords a light oil having a similar composition to that from the heavy oil and a hydrocarbon gas composed of the lower paraffins, which, after the removal of the by-products (water, ammonia, and hydrogen sulfide) has good burning properties. The formation of these paraffins can be ascribed to the generation of hydrogen within the system that occurs during the pyrolysis of condensed aromatic structures.

Although much work has been reported on the *thermal decomposition* of asphaltenes, a lesser amount of work is reported for the resins. The data that are available indicate that, like the asphaltenes, the resins can be decomposed thermally to produce, on the one hand, a hydrocarbon-type of distillate and, on the

other hand, cokelike material. The prevalent conditions determine the relative proportions of the two products.

Data from pyrolysis investigations and from HPLC-UV investigations show that the condensed aromatic hydrocarbon fragments in the resins and asphaltenes match those in the gas oil fraction. It now appears that the asphaltene constituents are not different types (i.e., polynuclear aromatic sheets containing 12 or more condensed rings) to the remainder of the oil. The asphaltene constituents are compatible with the structural types with the lower-molecular-weight fractions and also compatible with natural product origins of petroleum (Speight, 1986, 1994). It is however, in addition to the increasing molecular weight of the resin and asphaltenes constituents, the frequency of occurrence of the heteroatom functions that increases. This is the main difference between the constituents of the resin and asphaltenes fractions and the remainder of the constituents in petroleum.

The nonvolatile oil fraction is thermally stable at ordinary temperatures and is quite resistant to attack by many chemicals. At *elevated temperatures*, fission of side chains takes place. In the presence of oxygen (or air), carbon dioxide, water, and products containing carbonyl $>\text{C}=\text{O}$ and hydroxyl $-\text{O}-\text{H}$ groups are found. If the temperature is sufficiently high, the products containing oxygen functions are unstable and dehydrogenation is the overall result.

In pyrolysis, the simplest degradation method, the sample is rapidly heated under exclusion of air to a temperature high enough to break some of the chemical bonds. Typical reactions are dealkylation and the breakage of (aliphatic) sulfur-sulfur and sulfur-carbon bonds. The problem here is to find a compromise between specificity and yield, which means that the temperature and other reaction conditions must be carefully chosen.

A common procedure is to heat the sample in a tube to the desired temperature for several hours. The tube may be evacuated (Rubinstein and Strausz, 1987) or swept with an inert gas (McIntire et al., 1987). Typical temperatures reported for these procedures are 300–400°C (570–750°F), and sample sizes are in the order of 100 mg or less. The reaction products are collected in various ways and usually analyzed afterward. Only with gas-swept arrangements can the products be analyzed on-line by gas chromatography.

Flash pyrolysis on a thin, electrically heated wire with properly chosen Curie temperature, for example, 610°C (1130°F), ensures rapid warm-up and brief exposure time for suppression of side reactions. In this procedure, a very small amount (about 100 µg) of the sample is pressed onto the wire. Warm-up time is 0.1 s, and the gaseous products are directly transferred to a gas chromatograph, preferably with MS as detector.

Another variation of flash pyrolysis has been described (Payzant et al., 1991) in which the sample (in toluene solution) is dripped from a dropping funnel at a slow rate (<1 ml/min) to the bottom of a flask which is heated by a temperature-controlled sand bath, typically at 430°C (800°F). A flow of nitrogen sweeps the

reaction products and the solvent to a cooled collection flask for subsequent concentration and analysis. There was no evidence for degradation of the toluene. The pyrolysis oil can be separated into a number of compound groups by a combination of liquid chromatography with another associated physical identification or chemical method.

8.7. MISCELLANEOUS METHODS

Reactions of asphaltenes with sulfur have also received some attention and have yielded interesting results. For example, treatment of the asphaltenes with oxygen or with sulfur at 150–250°C (300–480°F) yields a condensed aromatic product [H/C = 0.97; H/C (asphaltenes) = 1.20] containing very little additional sulfur. The predominant reaction here appears to be condensation between the aromatic and aliphatic moieties of the asphaltenes promoted by elemental sulfur, which are in turn are converted to hydrogen sulfide. Condensation appears to proceed in preference to molecular degradation, and treatment of the condensed products at 200–300°C (390–570°F) for 1–5 h again affords good-grade cokes (H/C = 0.54–0.56). In all instances the final products contain only very low amounts of elements other than carbon and hydrogen (N + O + S < 5% by weight), a desirable property of good-grade coke.

Reductive alkylation is ordinarily used to make asphaltene constituents more soluble and less prone to aggregation in hydrocarbon solvents. The sample is dissolved in tetrahydrofuran (although not all asphaltene constituents are soluble in this solvent), an excess of metallic potassium under exclusion of air. Assuming no side reactions, this method produces the final alkylated product. However, it has been demonstrated (Ebert et al., 1989) that petroleum residues contain sufficient aromatic carbon to make the reaction proceed well without additional naphthalene. It is preferable to omit this agent because side reactions are then mitigated.

In contrast, it has been claimed (Ignasiak et al., 1977) that the presence of naphthalene in the reaction mixture increases the number of sulfur atoms removed and also the number of the alkyl groups inserted into the asphaltenes moieties. However, the absence or presence of naphthalene was not the only difference in the reaction conditions, and serious experimental flaws negated the experimental results (Speight and Moschopedis, 1980).

A principal reaction of this procedure is the conversion of aromatic double bonds via dianions to naphthenic bonds with alkyl groups inserted on to the corresponding carbon atoms. Two other important reactions are the desulfurization of thiophene structures and the cleavage and transalkylation of (aliphatic) sulfides. Such reactions cannot be ignored in the interpretation of the data.

A more elegant two-step reaction sequence has been developed for cleaving carbon-sulfur bonds (Rose and Francisco, 1987, 1988). Some carbon-carbon bonds

are also cleaved by the alkali metal, followed by selectivity labeling the resulting thiols with carbon-13 and deuterium-enriched groups. Carbon-13 and deuterium magnetic resonance spectroscopy of the samples before and after cleavage gave recognizable chemical shift data of the methyl labels, enabling identification of several types of S compounds in three main classes:

1. diaryl sulfides ranging from dibenzyl to bis(1-naphthylmethyl) sulfide,
2. sulfur compounds that form thiols on reductive protonation, namely, alkyl-aryl and aryl-aryl sulfides as well as certain hyphened derivatives, and
3. S compounds that resist cleavage by reductive protonation, for example, dibenzothiophene derivatives and dialkylsulfides.

This procedure allows a more specific identification of the chemistry of the various sulfur compounds and the means by which they will react under various conditions.

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CHAPTER

9

FRACTIONAL COMPOSITION

9.1. INTRODUCTION

Recognition that refinery behavior is related to the composition of the feedstock has led to a multiplicity of attempts to establish petroleum and its fractions as compositions of matter. As a result, various analytical techniques have been developed for the identification and quantification of *every molecule* in the lower-boiling fractions of petroleum. It is now generally recognized that the name *petroleum* does not describe a composition of matter but rather a mixture of various organic compounds that includes a wide range of molecular weights and molecular types that exist in balance with each other (Speight, 1994; Long and Speight, 1998). There must also be some questions of the advisability (perhaps *futility* is a better word) of attempting to describe *every molecule* in petroleum. The true focus should be to what ends these molecules can be used.

Thus investigations of the character of petroleum need to be focused on the influence of its character on refining operations and the nature of the products that will be produced. Furthermore, one means by which the character of petroleum has been studied is through its fractional composition. However, the fractional composition of petroleum varies markedly with the method of isolation or separation, thereby leading to potential complications (especially in the case of the heavier feedstocks) in the choice of suitable processing schemes for these feedstocks. Crude oil can be defined (on a *relative* or *standard* basis) in terms of three or four general fractions: asphaltenes, resins, saturates, and aromatics (Fig. 9.1). Thus it is possible to compare interlaboratory investigations and thereby apply the concept of predictability to refining sequences and potential products.

Investigations of the character of petroleum through fractionation studies have been practiced for more than 160 years (Boussingault, 1837), although modern fractionation techniques are essentially a twentieth century approach to examining petroleum composition (Rostler, 1965; Altgelt and Gouw, 1979; Altgelt and Boduszynski, 1994; Speight, 1999). In fact, the fractionation of petroleum has evolved to such an extent that it is now possible to determine with a high degree of accuracy the *types* of compounds present in a crude oil.

The fractionation methods available to the petroleum industry recognize the need to separate the constituents without alteration of their molecular structure,

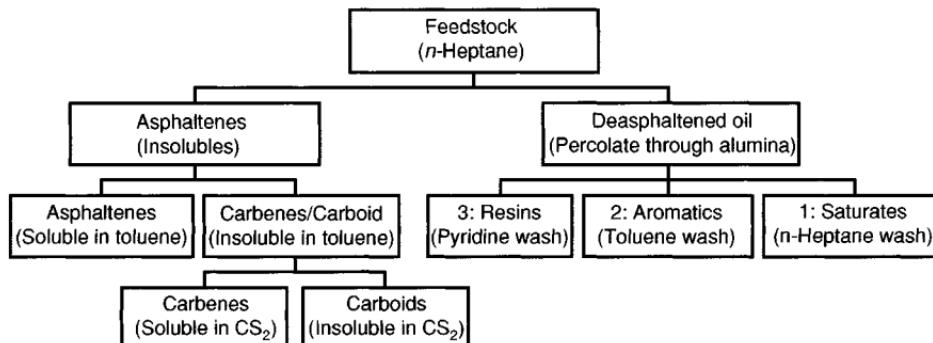


Figure 9.1. A simple fractionation scheme for various feedstocks.

thereby obtaining these constituents in a substantially pure state. Thus the general procedure is to use techniques that segregate the constituents according to molecular size and molecular type.

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

The order in which the several fractionation methods are used is determined not only by the nature and/or composition of the crude oil but also by the effectiveness of a particular process and its compatibility with the other separation procedures to be employed. Thus, although there are wide variations in the nature of crude oil (Chapters 1 and 2), there have been many attempts to devise standard methods of petroleum fractionation. However, the various laboratories are inclined to adhere firmly to and to promote their own particular methods. Recognition that no one particular method may satisfy all the requirements of petroleum fractionation is the first step in any fractionation study. This is mainly because of the complexity of petroleum, not only from the distribution of the hydrocarbon species but also from the distribution of the heteroatom (nitrogen, oxygen, and sulfur) species.

It is the purpose of this chapter to present an overview of those methods that have been applied to the separation of petroleum. This leads not only to an understanding

of the separation of petroleum but also to an understanding of the character of petroleum. Both factors bear a very strong relationship to the processability of petroleum (van Nes and van Westen, 1951; Traxler, 1961; Fisher, 1987; Speight, 1999).

9.2. DISTILLATION

Distillation is a common method for the fractionation of petroleum that is used in the laboratory as well as in refineries. The technique of distillation has been practiced for many centuries, and the stills that have been employed have taken many forms (Nelson, 1958; Gruse and Stevens, 1960; Speight, 1999). In the early days of the refining industry, distillation was recognized as a way to produce a desirable product (*kerosene* as a *lamp oil*). Thus it is not surprising that distillation became the process of choice for petroleum refining; this process has evolved from the simple distillation units to complex multiplate still used in the refining industry.

Distillation is the most basic separation process in a petroleum refinery. It has been proposed (Altgelt and Boduszynski, 1994) that distillation should have a similar place in the laboratory of the analytical petroleum chemist in that it should precede any other separation methods in most cases. However, the analytical chemist who focuses on petroleum may not be of a similar opinion when dealing with heavy oil and tar sand bitumen. There are methods for distillation of heavy oil or bitumen at very low pressures and, consequently, to a very high atmospheric equivalent boiling point; however, the gains must be weighed against the effort.

Nevertheless, where applicable, distillation reduces both the molecular weight range and the variety of chemical groups. However, separation by distillation takes place according to volatility and not necessarily according to molecular weight. Comparison of the boiling points of 2-hydroxypyridine (280°C/760 mm Hg, 535°F/760 mm Hg) and 4-hydroxypyridine (257°C/10 mm Hg, 495°F/10 mm Hg) illustrates that molecular structure and the consequences of this structure also influence boiling point. In more general terms, and without any attendant bonding influences, the boiling point increases with molecular weight in each homologous series, but the differences between boiling points in the different homologous series are quite substantial. For example, the two-ring naphthalene *decahydronaphthalene* (*decalin*) with 10 carbon atoms (molecular weight 138) boils at 195°C (383°F), but the 10-carbon-atom normal paraffin *decane* (molecular weight 142) boils at 174°C (345°F).

The theory of distillation has occupied several large texts and is discussed only briefly here. Thus, if a liquid is contained in a closed space, it emits vapor until a pressure of the vapor is reached that is related to the temperature of the system; the vapor is then said to be saturated. The vapor pressure of a liquid substance in contact with its own liquid is constant and is independent of the amount of liquid

and of the vapor present in the system. The vapor pressure is usually expressed in terms of the height of a mercury column (in millimeters or inches) that produces an equivalent pressure.

The vapor pressure of a liquid increases with increasing temperature; when the vapor pressure is equal to the total pressure exerted on the surface of the liquid, the liquid boils. Thus the boiling point of a liquid may be defined as the temperature at which the vapor pressure of the liquid is equal to the external pressure exerted on the liquid surface. This external pressure may be exerted by atmospheric air, by other gases, by vapor and air, and so on. The boiling point at a pressure of 760 mm air is usually referred to as the normal boiling point.

The boiling point of a pure liquid has a definite and constant value at a constant pressure, but the boiling point of an impure liquid depends to some extent on the nature of the impurities. If the impurities are nonvolatile, the liquid boils at a constant temperature and the impurities remain behind when the liquid has been distilled. If, however, the impurities are volatile, the boiling point rises gradually as the liquid distills or may remain constant at a particular stage of the distillation because of the formation of a constant boiling point mixture of two or more components.

The common feature of all distillation processes is the tendency for the concentration of the more volatile component in the vapor phase to be greater than that in the liquid phase when the two phases have been in contact. In simple distillation, the enrichment of the more volatile component is achieved by partially vaporizing a liquid mixture, either by raising the temperature or by reducing the pressure, and allowing the two phases to separate.

Thus the distribution of a component between vapor and solution may be expressed as a function of temperature and pressure. If an ideal solution contains components of different vapor pressures at a specific temperature, the vapor phase in equilibrium with the liquid phase at this temperature is relatively richer in the more volatile components. The liquid phase is relatively richer in the less volatile components and the components with lower vapor pressures, and a partial separation of components may be achieved. The vapor phase that separates is said to distill at this temperature, and a solution of continuous boiling points, such as petroleum, can be separated by multiple stages of distillation into *fractions*; each fraction has a relatively narrow boiling range but may, in fact, contain many constituents.

In the *chemical sense*, the difference between carbon number (or molecular weight), boiling point, and chemical composition is obvious. Thus *n*-paraffins have, for a given carbon number, the lowest boiling points. Naphthenes boil at somewhat higher temperatures, and aromatic hydrocarbons have higher boiling points. Alkyl substitution elevates the corresponding boiling point, and aromatic polar species have even higher boiling points. Condensed polynuclear aromatic molecules with several polar groups and no alkyl chains have the highest boiling points for a given molecular weight.

Thus a narrow distillation fraction can contain a wide range of molecular weight species. The different intermolecular forces that affect the heat of vaporization and thus the boiling point of a compound cause this important fact. For a homologous series of alkanes, the weak Van der Waals dispersion forces prevailing between the molecules become greater in proportion with increasing carbon number. Aromatic compounds have additional attractive intermolecular forces acting on them and, therefore, have higher boiling points than aliphatic molecules of similar molecular weight and structure. The intermolecular forces are even stronger in polar compounds, which are capable of hydrogen bonding or other types of polar interactions.

Among the prevalent distillation methods, there are two major categories: (1) column distillation and (2) short-path distillation (Chapter 5).

Column distillation (batch mode) is performed at high pressures, at atmospheric pressure, and at reduced pressures. High pressures are used mainly in large-scale refinery distillations with low-boiling distillates and result in higher distillation temperatures.

In *short-path distillation* (also called *molecular distillation*) (continuous mode), a very high vacuum is applied and the sample passes rapidly as a very thin film over a heated surface. The lighter molecules evaporate and are condensed on a cooled surface that is located within 2–3 cm of the condensing surface. The vacuum must be high enough to ensure that the mean free-path length of a distillate molecule is shorter than the distance between the heated and the cooled surfaces.

The bulk of the distillation procedures performed in the laboratory (Chapter 5) is carried out in packed columns. The efficiency of a distillation column is measured in terms of its number of theoretical trays or plates, and the higher this number, the higher its efficiency. Generally, the number of theoretical plates is proportional to the column length. For most column packings in laboratory distillations, the height of a theoretical plate is roughly equal to the diameter of the column.

A *theoretical plate* in distillation is a hypothetical section of a column that produces the same difference in composition of the ascending distillate as exists at equilibrium between a liquid mixture and its vapor. It acts as an ideal bubble-cap tray would. The packing provides a large surface area for the descending reflux. As the rising vapor comes in contact with the descending liquid, some of its higher-boiling component transfers to the reflux and some of the lower-boiling component transfers from the liquid to the vapor.

Therefore, the vapor arriving at the top of a theoretical plate section contains a lower amount of high-boiling material than it had when it came in at the bottom, and its lighter component is correspondingly enriched. On the other hand, the reflux leaving the theoretical plate at the bottom contains a higher amount of high-boiling material than when it came in at the top. Also, comparison of the composition of the liquid phase at the top with that of the liquid phase at the bottom shows that if the section indeed has the length of a theoretical plate, then the composition of the

liquid phase at its top is equal to the (theoretical) vapor composition in equilibrium with the liquid at the bottom.

9.2.1. Atmospheric Pressure

Distillation has found wide applicability in petroleum science and technology, but it is generally recognized that the fractions separated by distillation are only rarely, if at all, suitable for designation as a petroleum product. Each usually requires some degree of refining, which of course varies with the impurities in the fraction and the desired properties of the finished product. Nevertheless, distillation is the most important fractionating process for the separation of petroleum hydrocarbons; it is an essential part of any refinery operation (Nelson, 1958; Bland and Davidson, 1967).

However, insofar as petroleum is a mixture of several thousand (or even more) individual chemical compounds, there is little commercial emphasis on the isolation of the individual components. The aim of the distillation of petroleum is predominantly an assessment of the nature and volatility of the material through separation into several fractions of substantially broad boiling ranges.

The standard laboratory distillation column has a diameter of about 25–60 mm, a height of 1–1.5 m, and an efficiency of 15–50 theoretical plates. Occasionally, one may need taller columns or columns with a high-efficiency packing delivering as many as 70–100 theoretical plates.

Of special interest in the distillation laboratory are the *spinning band* columns. These are constructed of precision-bore glass tubing 1–20 mm in diameter and 30–100 cm in length, in which a closely fitted twisted Teflon or metal band rotates at high speed. The centrifugal force exerted on both the ascending vapors and the descending reflux brings both into intimate contact on the column walls, achieving the high mass and heat transfer required for good efficiencies. The major advantage of these columns is that they have very low pressure drops. They can be used for high-vacuum distillation of heavy oil and bitumen that have low or zero amounts of nonvolatile constituents up to boiling points of about 430–480°C (800–900°F).

In a refinery operation, there is a tendency to construct columns with a large number of theoretical plates and to operate them at a low reflux ratio to reduce heating and cooling costs. In the laboratory, there is the tendency to use less efficient columns to reduce column holdup and to compensate by running the unit at a higher reflux ratio. This, however, reduces the throughput. At a reflux-to-distillate ratio of $R:1$, each distillate molecule travels the column $R + 1$ times up and R times down on average before it is collected. Hence, a balance must be found between sufficiently high reflux ratios for good efficiency on the one hand and low enough reflux ratios for reasonable throughput rates on the other. Reflux ratios of 5:1 to 20:1 are commonly used in the laboratory.

9.2.2. Reduced Pressure

Separation of the *reduced crude* (*atmospheric residuum*) into the constituent fractions requires that the next-stage distillation be carried out under reduced pressure. The higher boiling constituents undergo thermal decomposition at temperatures above 350°C (660°F). This will result in molecular fragmentation leading to volatile products (which were not indigenous to the crude oil) and to coke.

In actual refinery practices, higher temperatures are used and, to avoid these thermal decomposition reactions, it is necessary to reduce the pressure at which the distillation is performed and to reduce the contact time or residence time of the feedstock in the hot zones. Because the vapor pressure and temperature are related, the lowering of the pressure is accompanied by a corresponding decrease in the boiling points of the individual constituents.

Thus vacuum distillation also allows the laboratory scientist or the refiner to obtain higher-boiling distillates, leaving a smaller amount of the residuum, without thermal decomposition. Operational pressures in vacuum distillation with packed columns generally range from 5 to 200 mm Hg. At lower pressures, the vapor velocity increases, resulting in greater pressure drops, and there may be little advantage in going to pressures below 5 mmHg.

For still lower pressures, an empty column or a spinning band column is necessary but not always practical in the refinery. With these columns, the pressure drop is small enough that low pressures can be maintained in the reboiler. For instance, with a distillate pressure of 0.1 mm Hg, one may have a pressure of 0.5–1 mm Hg in the reboiler that, theoretically, allows the collection of distillates with an atmospheric equivalent temperature cut point of as high as 560°C (1,050°F). The actual observed boiling points during this distillation are, of course much lower. Despite the low pressure, the reboiler may have to be heated as high as 370°C (700°F) for such high-boiling distillates.

From the actual boiling points, obtained at reduced pressure, the so-called atmospheric equivalent temperatures (AET), at which the material would boil under atmospheric pressure if it was stable and would not decompose, are calculated. Thus the concept of vacuum distillation, for which an atmospheric equivalent temperature is derived, extends the boiling point range of atmospheric distillation beyond the decomposition limit. It provides a common basis for the categorization and direct comparison of petroleum components across the entire volatility range accessible by atmospheric and vacuum distillation.

Within the distillates, the physical and chemical properties are known to change only gradually with the boiling point, allowing interpolations and even extrapolations with reasonable certainty. Whenever the range of distillates is expanded, first by vacuum distillation, then by short-path distillation, the new distillate portions of the previously *nondistillable* residua follow the same patterns as the previous distillates. The relationship of carbon number or molecular weight, or of sulfur and

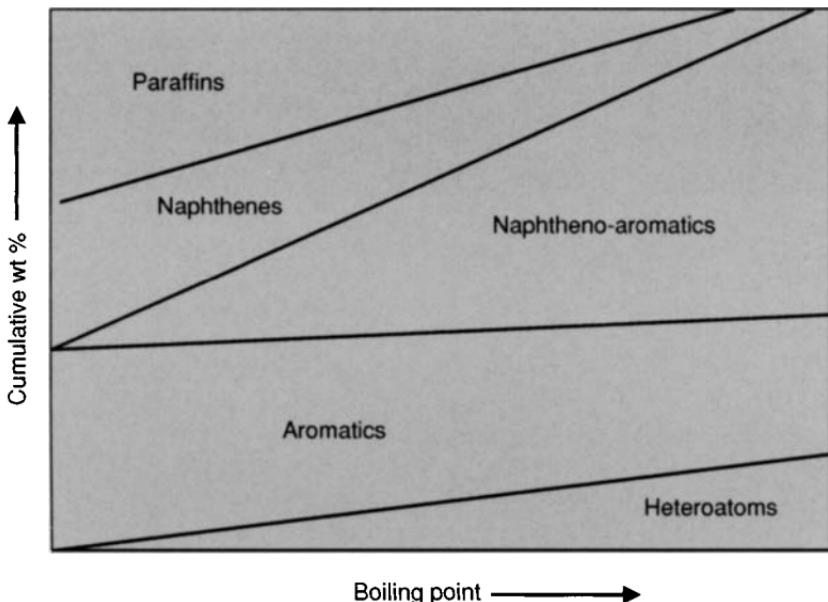


Figure 9.2. Representation of the volatile constituents of petroleum as a continuum.

nitrogen concentrations, could be extended smoothly into the new regions. Such continuity is no surprise but highly likely, considering the nature of the petroleum precursors and the maturation chemistry. Thus the data can be extrapolated across the dividing line between distillates and residua, even into those ranges that are still beyond exact measurements.

Indeed, the concept that petroleum is a continuum of structural types that may be further defined in terms of polarity and molecular weight (or boiling point) is not new and has been generally accepted for several decades (Chapter 15) (Long, 1981; Speight, 1999 and references cited therein). The initial focus in this concept was on the hydrocarbon types that occurred in the volatile fractions (Fig. 9.2), leaving the nature of the nonvolatile fractions open to speculation. Further work on nonvolatile gas oils has shown that the continuum is ubiquitous, at least sufficient to include such fractions (Fig. 9.3).

The concept that asphaltene fraction is located at the high-molecular-weight end of this continuum has also been postulated and is now becoming accepted (Speight, 1994). Similar reasoning is appropriate to the constituents of the resin fraction. In addition, there is evidence that the continuum of hydrocarbon types, or more correctly hydrocarbon fragments, continues from the gas oil fractions into the resins and asphaltenes.

The atmospheric equivalent temperature that is derived from earlier relationships of the midboiling point of petroleum fractions (Altgelt and Boduszynski,

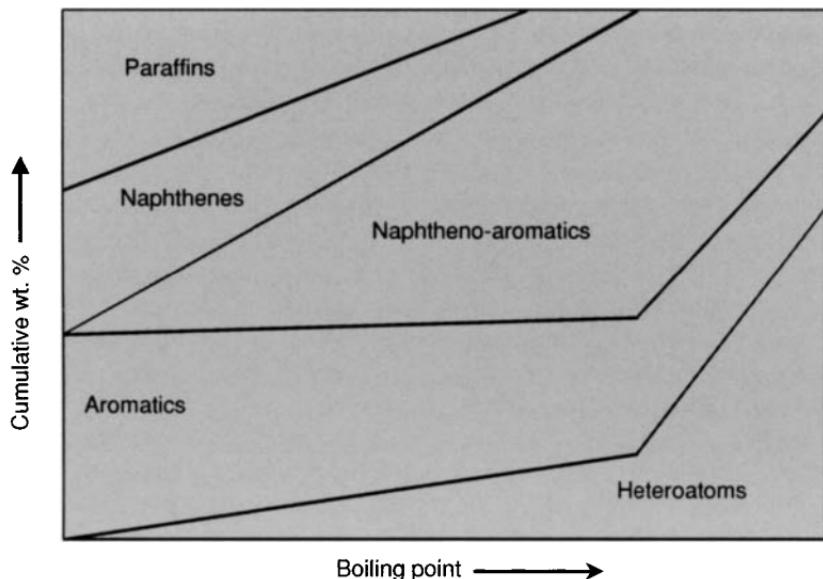


Figure 9.3. Representation of all of the constituents (volatile and nonvolatile) of petroleum as a continuum.

1994) can be estimated from the actual boiling points obtained under vacuum by the formula

$$AET(C) = [(748.1 \times A)/(1/VT,K) + (0.3861 \times A) - 0.00051606] - 273$$

$$A = [5.9991972 - (0.9774472 \times \log P)]/[2663.129 - (95.76 \times \log P_0)]$$

where VT,K is the observed vapor temperature in degrees Kelvin and P is the pressure of the system in mmHg observed when the vapor temperature was read. Atmospheric equivalent temperatures can be calculated, and the *true boiling point* (TBP) distribution of crude oil (*distillation profile*) can be derived (ASTM D-2892) (Chapter 5).

With the use of the atmospheric equivalent boiling point relationship (Altgelt and Boduszynski, 1994), it is possible to assign numbers to the boiling ranges of asphaltenes that are dependent on hydrogen-carbon atomic ratio and also on density (Table 9.1, Fig. 9.4). Similar boiling ranges can be estimated on the basis of hypothetical structures that have also been assigned to asphaltenes (Speight, 1994). These data show that any attempts at distillation of asphaltene constituents will present a formidable obstacle.

As an alternative to empty column or spinning band distillations or to cut even deeper into the stock, *high-vacuum short-path distillation* can be used. Other

**Table 9.1. Calculated Hypothetical Data for the Boiling Points (°F) of Asphaltenes
(see also Fig. 9.4)**

Mw	H/C In Increments of 0.05 From 1.00 to 1.30							
	Boiling Point	Boiling Point	Boiling Point	Boiling Point	Boiling Point	Boiling Point	Boiling Point	Boiling Point
1000	1485.792	1507.699	1528.888	1549.413	1569.323	1588.66	1607.463	
1100	1543.889	1566.653	1588.67	1609.998	1630.686	1650.779	1670.317	
1200	1597.914	1621.475	1644.263	1666.337	1687.749	1708.545	1728.767	
1300	1648.514	1672.821	1696.331	1719.103	1741.194	1762.648	1783.511	
1400	1696.185	1721.195	1745.384	1768.816	1791.545	1813.62	1835.085	
1500	1741.318	1766.993	1791.826	1815.881	1839.214	1861.877	1883.914	
1600	1784.224	1810.532	1835.977	1860.625	1884.533	1907.754	1930.334	
1700	1825.161	1852.072	1878.101	1903.314	1927.772	1951.525	1974.623	
1800	1864.34	1891.829	1918.416	1944.171	1969.153	1993.416	2017.01	
1900	1901.937	1929.981	1957.104	1983.378	2008.864	2033.617	2057.686	
2000	1938.104	1966.681	1994.32	2021.094	2047.064	2072.288	2096.815	
2100	1972.97	2002.06	2030.197	2057.452	2083.89	2109.567	2134.536	
2200	2006.645	2036.232	2064.849	2092.569	2119.458	2145.574	2170.968	
2300	2039.226	2069.293	2098.375	2126.545	2153.871	2180.411	2206.217	
2400	2070.798	2101.331	2130.863	2159.469	2187.218	2214.168	2240.375	
2500	2101.435	2132.42	2162.389	2191.419	2219.578	2246.927	2273.521	

names for this technique are molecular distillation and/or *wiped-film distillation*, although the latter is often performed with insufficient vacuum and belongs then to a different category.

The most important feature of the short-path still is a very high vacuum of at least 10^{-3} mmHg that ensures that the mean free-path length of the molecules in the gas phase is approximately 2–3 cm, which is the distance between the evaporator and the condenser surfaces. These conditions afford much lower distillation temperatures than possible in regular open columns at the same surface temperature. The sample is spread into a very thin film on the evaporating surface for quick evaporation and a short residence time. The combination of high vacuum, short distance, and short residence time allows very deep distillation without decomposition. Modern versions of these short-path stills can fractionate oils up to atmospheric equivalent boiling points of 700°C (1,300°F) with fairly high throughput rates. The small DISTACT laboratory short-path still, for example, has a rate of about 100–800 ml/h with a residence time of less than 1 min. Large production plants can operate with throughputs of up to 300 L/m²/h.

In short-path stills (Chapter 5), the preheated sample is pumped at a precisely regulated rate onto the surface of a heated vertical cylinder in the evaporation

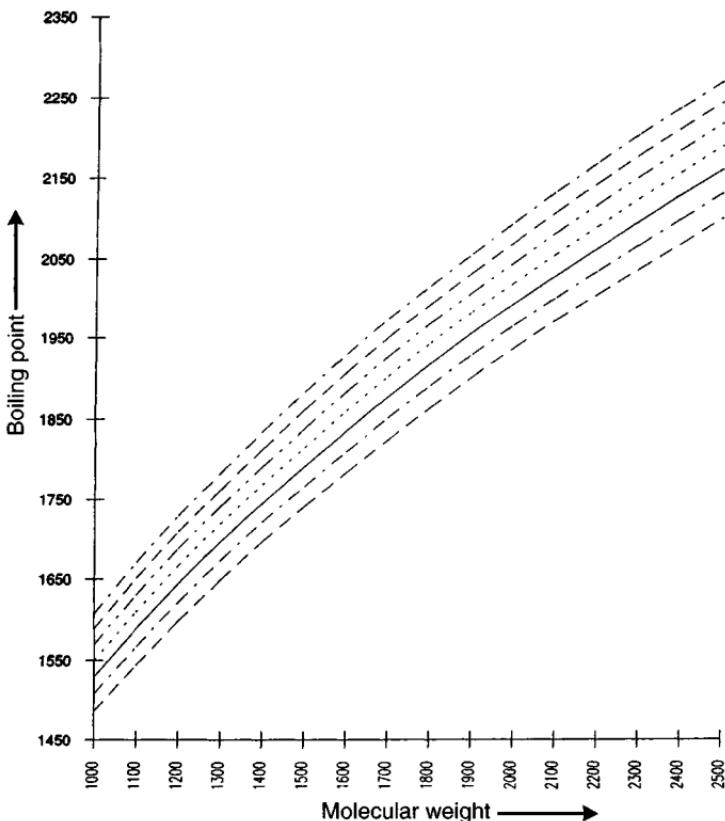


Figure 9.4. Representation of the hypothetical boiling points ($^{\circ}\text{F}$) of asphaltenes (see also Table 9.1).

chamber where it is spread by wipers into a uniform, thin, falling (downward flowing) film. The lower-boiling components are flash-evaporated and collected on a condenser, typically a coil inside the feed cylinder, and only two fractions are produced, the flash distillate and the residue.

9.2.3. Azeotropic and Extractive Distillation

Should the separation of individual components from petroleum itself or from petroleum products be advantageous, there are means by which this can be accomplished. For example, when a constant-boiling mixture of hydrocarbons contains components whose vapor pressure is affected differently by the addition of, say, a nonhydrocarbon compound, distillation of the hydrocarbon mixture in the presence of nonhydrocarbon additive may facilitate separation of the hydrocarbon components.

In general, the nonhydrocarbon additive is a polar organic compound and should also have the ability to form a binary minimum constant-boiling (or azeotropic) mixture with each of the hydrocarbons. Thus it is often possible to separate compounds that have very close boiling points by means of azeotropic distillation.

However, when the added compound is relatively nonvolatile, it exists almost entirely in the liquid phase, and the process is actually extractive distillation.

The separation of petroleum by distillation into *fractions* results in a concentration effect in which the heteroatom constituents (metals included) occur for the most part in the residua (Long and Speight, 1990; Reynolds, 1998). Sulfur, because of its ubiquitous molecular nature, is often an exception to this generalization and occurs in most distillation fractions.

9.3. SOLVENT TREATMENT

Fractionation of petroleum by distillation is an excellent means by which the volatile constituents can be isolated and studied. However, the nonvolatile residuum, which may actually constitute from 1 to 60% of the petroleum, cannot be fractionated by distillation without the possibility of thermal decomposition; as a result, alternative methods of fractionation have been developed. However, those methods, which are designed to estimate sediment in crude oil products, are not discussed here. They are the subjects of another chapter (Chapter 13).

The treatment of petroleum and petroleum products with solvents varies from the more simple determination of the precipitation number of lubricating oils (ASTM D-91) to the more complex fractionation methods by which several constituent fractions are produced using methods that are reproducible and repeatable. In fact, it is often the simpler methods of testing that have led to the modern complex fraction procedures.

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

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

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

$$K = C_1/C_2$$

where C_1 and C_2 are the concentrations in the various phases. The distribution coefficient is usually constant and may vary only slightly, if at all, with the concentration of the other components. In fact, the distribution coefficients may differ for the various components of the mixture to such an extent that the ratio of the concentrations of the various components in the solvent phase differs from that in the original petroleum; this is the basis for solvent extraction procedures.

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

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

The list of compounds that have been suggested as selective solvents for the fractionation of petroleum is very large (Nelson, 1958; Gruse and Stevens, 1960; Speight, 1999). However, before any extraction process is attempted, it is necessary to consider the following criteria:

The differences in the solubility of the petroleum constituents in the solvent should be substantial.

The solvent should be significantly less or more dense than the petroleum (product) to be separated to allow easier countercurrent flow of the two phases.

Separation of the solvent from the extracted material should be relatively easy.

It may also be advantageous to consider other properties, such as viscosity, surface tension, and the like, as well as the optimal temperature for the extraction process. Thus aromatics can be separated from naphthene and paraffinic hydrocarbons by the use of selective solvents. Furthermore, aromatics with differing numbers of aromatic rings that may exist in various narrow boiling fractions can also be effectively separated by solvent treatment.

9.3.1. Asphaltene Separation

9.3.1.1. Influence of Solvent Type

The suggestion arose in 1914 that the systematic separation of petroleum be effected by treatment with solvents. If chosen carefully, solvents effect a separation between the constituents of residua, bituminous materials, and virgin petroleum according to differences in molecular weight and aromatic character. The nature and the quantity of the components separated depend on the conditions of the experiment, namely, the degree of dilution temperature and the nature of the solvent (Mitchell and Speight, 1973; Speight et al., 1984).

On the basis of the solubility in a variety of solvents, it has become possible to distinguish among the various constituents of petroleum and bitumen (Fig. 9.1). Crude oil generally does not contain *carboids* and *carbenes*. Residua from cracking processes may contain 2% w/w by weight or more. In fact, some of the highly paraffinic crude oils may contain only small portions of asphaltenes.

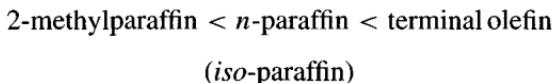
Thus the separation of crude oil into two fractions, asphaltenes and maltenes, is conveniently brought about by means of low-molecular-weight paraffinic hydrocarbons (ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, IP 143), which were recognized to have selective solvency for hydrocarbons and simple, relatively low-molecular-weight heteroatom derivatives. The more complex, higher-molecular-weight compounds are precipitated particularly well by addition of 40 volumes of *n*-pentane or *n*-heptane in the methods generally preferred at present (Speight, et al., 1984; Speight, 1994), although hexane is used on occasion (Yan et al., 1997). This process is no doubt a separation of the chemical components with the most complex structures from the mixture, and this fraction, which should correctly be called *n-pentane asphaltenes* or *n-heptane asphaltenes*, is qualitatively and quantitatively reproducible (Fig. 9.1).

One of the standard methods (ASTM D-2006) has been discontinued as an ASTM method but still finds use in many laboratories and represents a very convenient method of asphaltene separation.

If the precipitation method (deasphalting) involves the use of a solvent and a residuum or bitumen and is essentially a leaching of the deasphalted oil from the insoluble residue, this process may be referred to as *extraction*. However, under the prevailing conditions now in laboratory use, that is, using conventional petroleum or heavy oil or a solution of the residuum or bitumen in toluene (or a similar solvent), the term *precipitation* is more correct and descriptive of the method.

Variation in the solvent type also causes significant changes in asphaltene yield. For example, branched-chain paraffins or terminal olefins do not precipitate the same amount of asphaltenes as the corresponding normal paraffins (Mitchell and Speight, 1973). The solvent power of the solvents (i.e., the ability of the solvent

to dissolve asphaltenes) increases in the order



Cycloparaffins (naphthenes) have a remarkable effect on asphaltene yield and give results totally unrelated to those from any other nonaromatic solvent. For example, when cyclopentane, cyclohexane, or their methyl derivatives are employed as precipitating media, only about 1% of the material remains insoluble.

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

Thus the solvent power of nonpolar solvents has been expressed as a solubility parameter, δ , and equated to the internal pressure of the solvent, that is, the ratio between the surface tension γ and the cubic root of the molar volume V :

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

Alternatively, the solubility parameter of nonpolar solvents can be related to the energy or vaporization ΔE^v and the molar volume:

$$\delta_2 = (\Delta E^v/V)^{1/2}$$

or

$$\delta_2 = (\Delta H^v - RT/V)^{1/2}$$

where ΔH^v is the heat of vaporization, R is the gas constant, and T is the absolute temperature.

Consideration of this approach shows that there is indeed a relationship between the solubility parameters for a variety of solvents and the amount of precipitate (Mitchell and Speight, 1973). The introduction of a polar group (heteroatom function) into the molecule of the solvent has significant effects on the quantity of precipitate. For example, treatment of a residuum with a variety of ethers or treatment of asphaltenes with a variety of solvents illustrates this point (Speight, 1979). In the latter instance, it was not possible to obtain data from addition of the solvent to the whole feedstock per se, because the majority of the nonhydrocarbon materials were not miscible with the feedstock. It is nevertheless interesting that, as with the hydrocarbons, the amount of precipitate, or asphaltene solubility, can be related to the solubility parameter.

The solubility parameter allows an explanation of certain apparent anomalies, for example, the insolubility of asphaltenes in pentane and the near-complete

Table 9.2. Various Methods for Asphaltene Separation

Method	Deasphalting Liquid	Volume, ml/g
ASTM D-893	<i>n</i> -pentane	10
ASTM D-2006	<i>n</i> -pentane	50
ASTM D-2007	<i>n</i> -pentane	10
IP 143	<i>n</i> -heptane	30
ASTM D-3279	<i>n</i> -heptane	100
ASTM D-4124	<i>n</i> -heptane	100

solubility of the materials in cyclopentane. Moreover, the solvent power of various solvents is in agreement with the derivation of the solubility parameter; for any one series of solvents, the relationship between amount of precipitate (or asphaltene solubility) and the solubility parameter, δ , is quite regular.

In any method used to isolate asphaltenes as a separate fraction, standardization of the technique is essential. For many years, the method of asphaltene separation was not standardized, and even now it remains subject to the preferences of the standards organizations of different countries. The use of both *n*-pentane and *n*-heptane has been widely advocated, and, although *n*-heptane is becoming the deasphalting liquid of choice, this is by no means a hard-and-fast rule. In addition, it must be recognized that large volumes of solvent may be required to effect a reproducible separation, similar to amounts required for consistent asphaltene separation. It is also preferable that the solvents be of sufficiently low boiling point that complete removal of the solvent from the fraction can be effected, and, most important, the solvent must not react with the feedstock. Hence, the preference for hydrocarbon liquids, although the several standard methods that have been used are not unanimous in the ratio of hydrocarbon liquid to feedstock (Table 9.2).

n-Pentane and *n*-heptane are the solvents of choice in the laboratory (other solvents can be used; Speight, 1979) and cause the separation of asphaltenes as brown-to-black powdery materials. In the refinery, supercritical low-molecular-weight hydrocarbons (e.g., liquid propane, liquid butane, or mixtures of both) are the solvents of choice and the product is a semisolid (tacky) to solid asphalt. The amount of asphalt that settles out of the paraffin-residuum mixture depends on the size of the paraffin, the temperature, and the paraffin-to-feedstock ratio (Fig. 9.5) (Girdler, 1965; Corbett and Petrossi, 1978; Speight et al., 1984).

Insofar as industrial solvents are very rarely one compound, it was also of interest to note that the physical characteristics of two different solvent types, in this case benzene and *n*-pentane, are additive on a mole-fraction basis (Mitchell and Speight, 1973) and also explain the variation of solubility with temperature. The

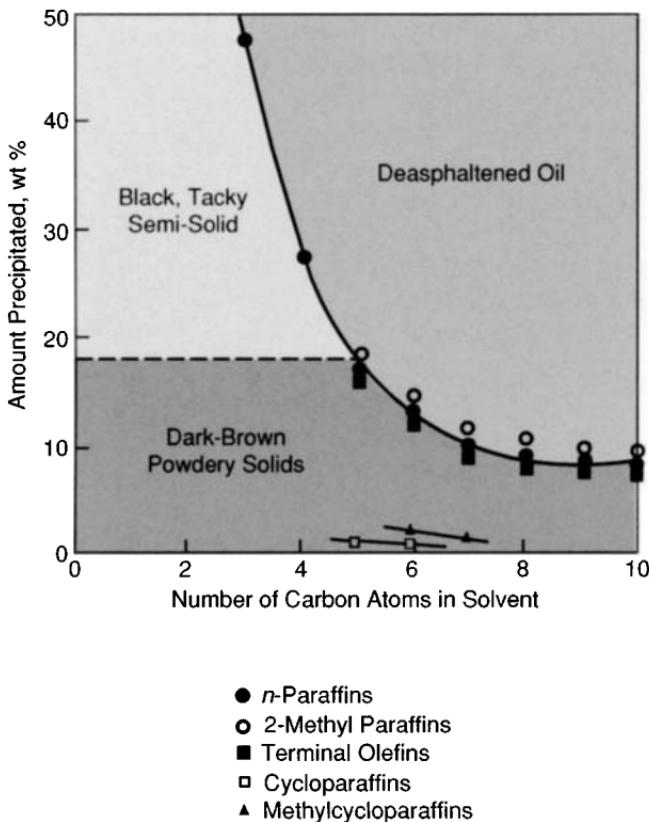


Figure 9.5. Variation of asphaltene yield with hydrocarbon liquid type.

data also show the effects of blending a solvent with the bitumen itself and allowing the resulting solvent-heavy oil blend to control the degree of bitumen solubility. Varying proportions of the hydrocarbon alter the physical characteristics of the oil to such an extent that the amount of precipitate (asphaltenes) can be varied accordingly within a certain range.

9.3.1.2. Influence of Degree of Dilution

One of the asphaltene separation methods (ASTM D-893) was developed for a specific test to determine the amount of insoluble material in lubricating oil. Another (ASTM D-2007) was designed for use with rubber extending and processing oils. Both tests recommend use of 10 ml of hydrocarbon liquid per gram of feedstock. This is not recommended in the tests that are now considered standard for asphaltene separation (ASTM D-3279, ASTM D-4124) (Speight et al., 1984).

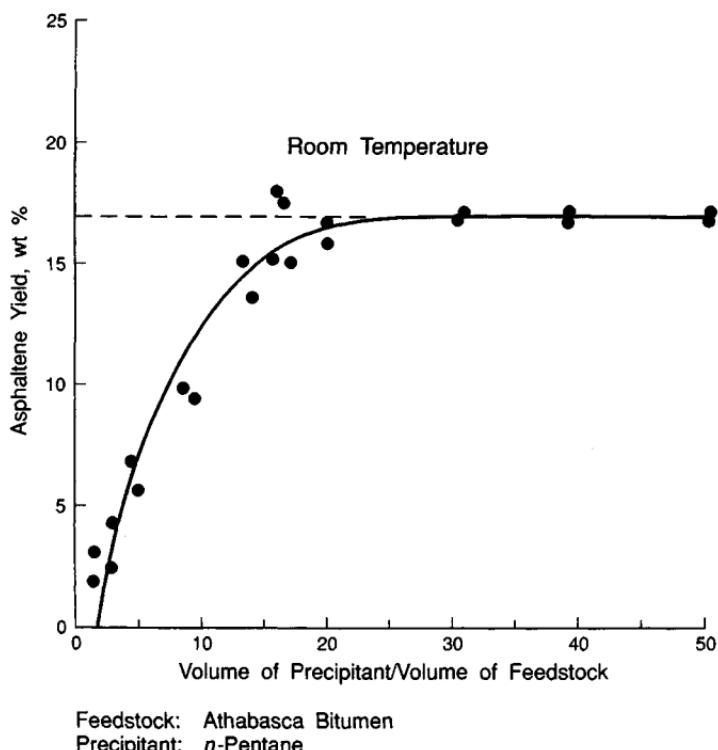


Figure 9.6. Variation of asphaltene yield with hydrocarbon-to-feedstock ratio.

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

At constant temperature, the quantity of precipitate first increases with increasing ratio of solvent to feedstock and then reaches a maximum (Fig. 9.6). Depending on the feedstock, there is a *solvent induction volume* in which little or no asphaltenes are precipitated. Very few data have been reported that relate to this aspect of asphaltene separation. The author has fragmentary evidence to show that the most polar materials (not necessarily the highest-molecular-weight material) separate first from the feedstock. This is in keeping with the increased paraffinicity of the feedstock as the hydrocarbon is added.

9.3.1.3. Influence of Temperature

When pentane and the lower-molecular-weight hydrocarbon solvents are used in large excess, the quantity of precipitate and the composition of the precipitate

changes with increasing temperature (Mitchell and Speight, 1973; Andersen, 1994).

One particular example is the separation of asphaltenes from using *n*-pentane. At ambient temperatures ($\sim 21^\circ\text{C}$, 70°F), the yield of asphaltenes is 17% w/w; however, at 35°C (95°F), 22.5% by weight asphaltenes are produced using the same feedstock-pentane ratio. This latter precipitate is in fact asphaltenes plus resins; similar effects have been noted with other hydrocarbon solvents at temperatures up to 70°C (160°F). These results are self-explanatory when it is realized that the heat of vaporization ΔH^ν and the surface tension γ , from which the solubility parameters are derived, both decrease with increasing temperature.

9.3.1.4. Influence of Contact Time

Contact time between the hydrocarbon and the feedstock also plays an important role in asphaltene separation (Fig. 9.7; Speight et al., 1984). Yields of the asphaltenes reach a maximum after approximately 8 h, which may be ascribed to the time required for the asphaltene particles to agglomerate into particles of a *filterable size* as well as the diffusion-controlled nature of the process. Heavier feedstocks also need time for the hydrocarbon to penetrate their mass.

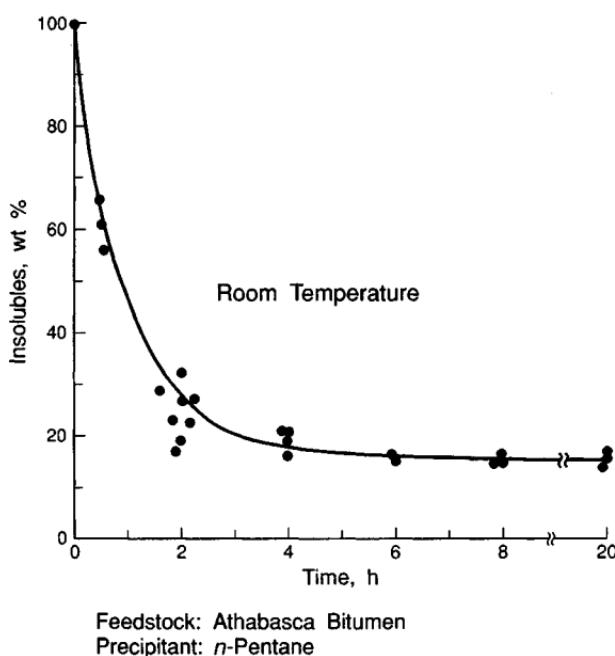


Figure 9.7. Variation of asphaltene yield with hydrocarbon-feedstock contact time.

9.3.2. Fractionation

After removal of the asphaltene fraction, further fractionation of petroleum is also possible by variation of the hydrocarbon solvent. For example, liquefied gases, such as propane and butane, precipitate as much as 50% by weight of the residuum or bitumen. The precipitate is a black, tacky, semisolid material, in contrast to the pentane-precipitated asphaltenes, which are usually brown, amorphous solids. Treatment of the propane precipitate with pentane then yields the insoluble brown, amorphous asphaltenes and soluble, near-black, semisolid resins, which are, as near as can be determined, equivalent to the resins isolated by adsorption techniques (Chapter 4).

There are also claims that solvent treatment at low temperatures (-4 to -20°C , 25 to -4°F) brings about fractionation of the maltenes. The hydrocarbon solvents pentane and hexane have been claimed adequate for this purpose but may not be successful with maltenes from bitumen or from residua. The author has had considerable success using acetone at -4°C (25°F) for the fractionation of maltenes from material other than cracked residua.

Other miscellaneous fractionation procedures for the deasphaltened oil involving the use of solvents are available (Speight, 1999). One method includes a procedure using polar solvents for separation into five fractions. These fractions are

1. hard resins, insoluble in 80:20 iso-butyl alcohol-cyclohexane mixture;
2. waxes, insoluble in a 1:2 mixture of acetone and methylene chloride at 0°C (-18°F);
3. soft resins, insoluble in iso-butyl alcohol; and
4. an oil fraction, the balance of the sample that remains soluble in iso-butyl alcohol.

The only drawback to this particular scheme appears to be the use of hexane as the precipitating medium. Use of this solvent does not completely precipitate the asphaltenes in a sample, and perhaps the fraction designated *hard resins* may contain considerable portions of asphaltenes.

A fractionation procedure was also devised using *n*-butanol and acetone as the solvents, but the preliminary separation of the asphaltenes was incomplete. The method consisted of (1) separation of an *asphaltic fraction* by *n*-butanol and (2) separation of the butanol-soluble portion into a *paraffinic fraction* and a *cyclics fraction* by chilling an acetone solution of the two, but it has the unfortunate result that all three fractions obtained may contain asphaltenes. It is difficult to compare the method with any other or even establish any correlation with previous experience. Even precipitation of the asphaltenes with *n*-pentane and subtraction of the asphaltenes from the asphaltic fraction, arriving at a fourth fraction (*asphaltic*

resins), did not appear to correct the faults of the method, because the asphaltic fraction does not contain all the asphaltenes of the specimen.

Another method of fractionating the deasphalted oil consisted of stepwise separation into the following fractions:

1. resins, *precipitated with propane and subdivided by fractionation with aniline into soft resins and hard resins,*
2. wax, *precipitated with methyl iso-butyl ketone, and*
3. oils, *remaining fraction separated with acetone into paraffinic oils and naphthenic oils.*

A strong feature of this method is the subdivision of the resins fraction by solubility in aniline and the subdivision of the paraffinic fraction into the three components: wax, paraffinic oils, and naphthenic oils.

It is unfortunate that, with the exception of asphaltene precipitation, no standard method exists for the fractionation of crude oil, residua, and bitumen, by solvent treatment. The procedures described here each have their own individual merits, but there has not been any serious effort to apply these methods to a wide variety of carbonaceous liquids to assess their general applicability. Fractionation by means of solvents alone (perhaps with the exception of propane, which requires pressure equipment) would be convenient indeed, provided that facile separation of the solvent and the products could be achieved at a later stage.

Another all-solvent procedure involves the use of acetone, which discharges a resin fraction, and dimethylformamide, which then discharges the saturates fraction.

The use of all-solvent methods for the separation of petroleum allows the fractionation of feedstocks to be achieved without loss of material (on the adsorbent) and produces fractions of varying polarity. The obvious benefit of the all-solvent techniques is the complete recovery of material, thereby allowing a more quantitative and qualitative examination of the feedstocks.

The disadvantages of an all-solvent separation technique are that, first, low temperatures (e.g., 0 to -10°C and the like) are advocated as a means of effecting oil fractionation with solvents (Rostler, 1965; Speight, 1979). Such requirements may cause inconvenience in a typical laboratory operation by requiring a permanently cool temperature during the separation. Second, it must be recognized that large volumes of solvent may be required to effect a reproducible separation in the same manner as the amounts required for consistent asphaltene separation (ASTM D-2006, ASTM D-2007, ASTM D-4124, ASTM D-893; IP 143). Finally, it is also essential that the solvent be of sufficiently low boiling point so that complete removal of the solvent from the product fraction can be effected. Although not specifically included in the three main disadvantages of the all-solvent approach,

it should also be recognized that the solvent must not react with the feedstock constituents. In addition, caution is still required to ensure that there is no interaction between the solvent and the solute.

9.4. ADSORPTION

The analysis of petroleum for the elemental composition or a convenient but meaningful physical property (Chapter 4) is generally considered to be the first step in characterization. The next step is to separate petroleum into its constituent compound groups and compound classes. Thus separation procedure are an analytical tool in themselves in that they yield information about feedstock composition in terms of its main compound groups and compound classes. The concentration of saturates, aromatics, and polar species (resins and asphaltenes) in a feedstock may be all the information required. Beyond that point, each of the four fractions may be further divided, for example, the aromatics by aromatic ring number into the compound classes of mono-, di-, tri-, tetra-, and penta-aromatics.

An important aspect of the application of separation procedures is the fact that the separation of a petroleum fraction into compound classes assists subsequent measurements performed for molecular characterization. Some molecular characterization procedures (Chapter 11) cannot be effectively applied to broad fractions, and further separation into subfractions is necessary. For example, a molecular ion peak can represent several compound types or even various compound classes rather than just one compound type, which makes its assignment difficult or impossible. Only mass peaks from well-defined fractions can be assigned unequivocally.

Careful separation provides such well-defined fractions for good mass spectra and the additional analytical information necessary for their interpretation. Chromatographic separation into well-defined compound-class fractions also facilitates the interpretation of other spectra, for example, from nuclear magnetic resonance and infrared spectroscopy (Chapter 7).

Another advantage of good separations is the mitigation of *peak crowding*. Crowded mass spectra are hard to read for two reasons: (1) because of peak overlap resulting from several different compound type molecules with similar masses and (2) because of dilution, which prevents some compounds from being seen and distinguished from the background noise. The dilution by other components in broad fractions is especially severe for molecules of high molecular weight. Although the latter may have reasonable concentrations in terms of weight percent, their mole percent, which determines the peak height in mass spectra, may be prohibitively low. Both advantages of good separations, the gain of complementary information and the avoidance of the dilution effect, are not restricted to mass spectrometry but are important when other molecular identification techniques are applied.

As already stated (Chapter 2), petroleum is a complex mixture of paraffin, naphthene, and aromatic hydrocarbons as well as nitrogen-, oxygen-, and sulfur-containing compounds, and traces of a variety of metal-containing compounds and the amounts of nonhydrocarbon compounds increase with molecular weight. The distribution of the constituents of petroleum varies with the petroleum but can generally be represented as consisting of the various hydrocarbon species with varying amounts of heteroatom species (Fig. 9.3).

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

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

However, depending on the adsorbent employed for the separation, a compound having an aromatic ring (i.e., 6 aromatic carbon atoms) carrying side chains consisting in toto of more than six carbon atoms (i.e., more than 6 nonaromatic carbon atoms) will appear in the aromatic fraction.

The typical *nitrogen compounds* found in petroleum are generally divided into two groups, basic and nonbasic (Chapter 2), each of which has alkyl chains and other ring systems. The basic nitrogen compounds cause difficulty with the many acid-catalyzed processes used in petroleum refining. For example, in catalytic cracking, the basic nitrogen adsorbs on the catalytic acid sites and reduces the cracking activity of the catalyst. Furthermore, in reactions catalyzed by liquid acids, the presence of basic nitrogen compounds in the feed increases acid consumption and thus the cost of the process. Typical of such processes are alkylation, isomerization, and olefin absorption.

Another type of nitrogen compound is the *porphyrins* (Chapter 2), which consist of four pyrrole rings connected together with methylene bridges at the carbons next to the nitrogen atoms. They are normally found in trace quantities in the high-molecular-weight fractions of petroleum as metal complexes.

The *oxygen compounds* found in petroleum fractions are often products of exposure to air. However, some naturally occurring oxygenated compounds do exist in petroleum; these are typically phenols, naphthenic acids, and esters (Chapter 2).

They increase in quantity and complexity as molecular weight increases, just as sulfur and nitrogen compounds do.

A variety of *sulfur compounds* occur in petroleum (Chapter 2) and include mercaptans ($-SH$), sulfides ($-S-$), and disulfides ($-S-S-$). They are much less thermally stable than the thiophene derivatives and often lose hydrogen sulfide on heating. They can also react thermally to form more stable sulfur compounds. In the chromatographic separation, these sulfur compounds are found in the polar aromatic fraction, even though they may not all be aromatic. *Thiophenes* tend to exhibit aromatic behavior and are collected with the aromatics when adsorption separation is used on petroleum fractions.

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

Numerous factors randomly affect the process of migration through a bed; in fact, the total distance traveled in a given time by different molecules of the same material is not constant. Nevertheless, the suitable choice of a bed and a moving (solvent) phase allows adequate separation of even multicomponent mixtures to be achieved.

The fractionation of petroleum components by adsorption on such materials as fuller's earth, animal charcoal, and various types of clay dates back to the beginning of the twentieth century. These materials effect an arbitrary separation of the material into a number of fractions that have variously been described as *oil*, *resins*, *hard resins*, and *soft resins*, to mention only the more commonly used terms.

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

Nevertheless, careful monitoring of the experimental procedures and the nature of the adsorbent have been responsible for the successes achieved with this particular technique. Early procedures consisted of warming solutions of the petroleum fraction with the adsorbent and subsequent filtration. This procedure has continued to the present day, and separation by adsorption is used commercially in plant operations in the form of clay treatment of crude oil fractions and products (Speight, 1999).

In the laboratory, very little use is made of the technique of warming a solution of the sample with the adsorbent. Rather, a chromatographic technique is employed in which the sample is washed through a column of the adsorbent using various solvents.

Numerous methods have been employed for the separation of petroleum fractions into the main compound groups such as saturates, aromatics, and polar species (Altgelt and Gouw, 1979; Altgelt and Boduszynski, 1994; Speight, 1999). However, it is generally recognized that the asphaltenes are first removed by the addition of a low-boiling liquid hydrocarbon (page 236) after which it is the deasphalted oil that is separated by adsorption techniques.

However, if the adsorption technique is performed using only one column (e.g., a silica column or an alumina column), separation is poor. There is frequent overlap of the various fractions. The saturate fraction may be contaminated with substantial amounts of the constituents of the aromatics, the aromatic fraction may be contaminated with constituents from the polar (resin) fraction, and the polar fraction may be contaminated with constituents of the aromatic fraction.

Thus procedures have evolved in which, after removal of the asphaltenes, the polar (resin) fraction is removed from the deasphalted oil first by use of a low-polarity adsorbent. This assists subsequent separations of the remaining neutral oil fraction (the combined aromatic and saturate fractions) using other adsorbents or clean columns by preventing the columns used in the latter process from being deactivated and destroyed by irreversible adsorption of the (polar) resin constituents. The neutral oil fraction can then more easily and cleanly be separated into saturates, aromatics, and (if necessary) into neutral heterocompounds.

9.4.1. ASTM Methods

There are three standard (ASTM) methods that provide for the separation of a feedstock into four or five constituent fractions (see Figs. 9.8, 9.9, 9.10, 9.11, and 9.12). It is interesting to note that, as the methods have evolved, there has been a change from the use of pentane (ASTM D-2006 and D-2007) to heptane (ASTM D-4124) to separate asphaltenes. This is, in fact, in keeping with the production of a more consistent fraction that represents the higher-molecular-weight, more complex constituents of petroleum (Girdler, 1965; Speight et al., 1984; Speight, 1999).

Two of the methods (ASTM D-2007 and D-4124) use adsorbents to fractionate the deasphalted oil, but the third method (ASTM D-2006) advocates the use of various grades of sulfuric acid to separate the material into compound types. Caution is advised in the application of this method because the method does not work well with all feedstocks. For example, when the *sulfuric acid* method (ASTM D-2006) is applied to the separation of heavy feedstocks, complex emulsions can be produced.

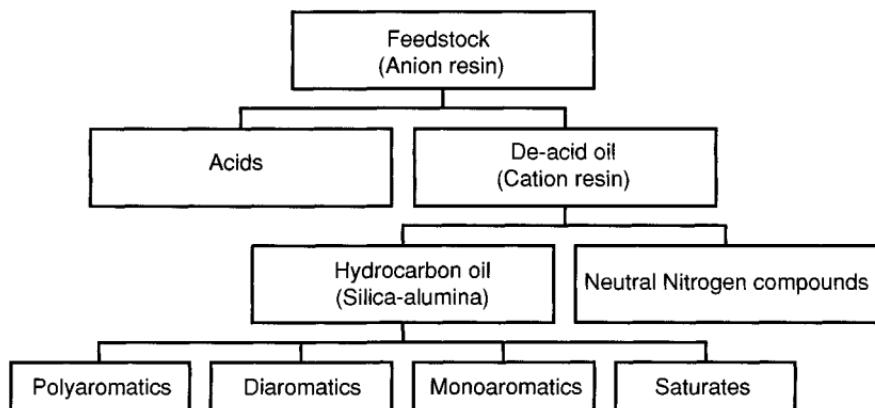


Figure 9.8. The USBM-API fractionation procedure.

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

In summary, the terminology used for the identification of the various methods might differ. However, in general terms, group-type analysis of petroleum is

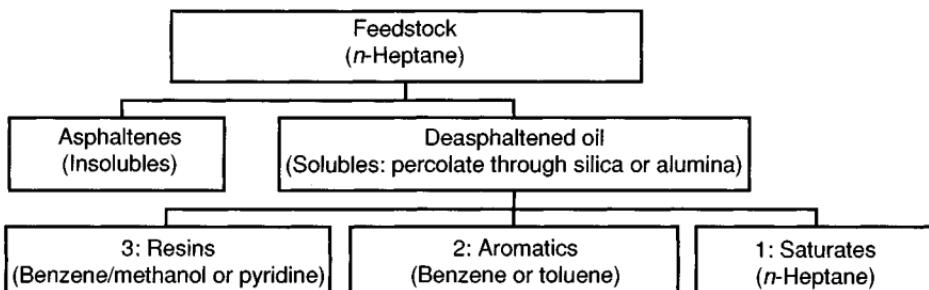


Figure 9.9. A simplified alternate procedure to the USBM-API fractionation method.

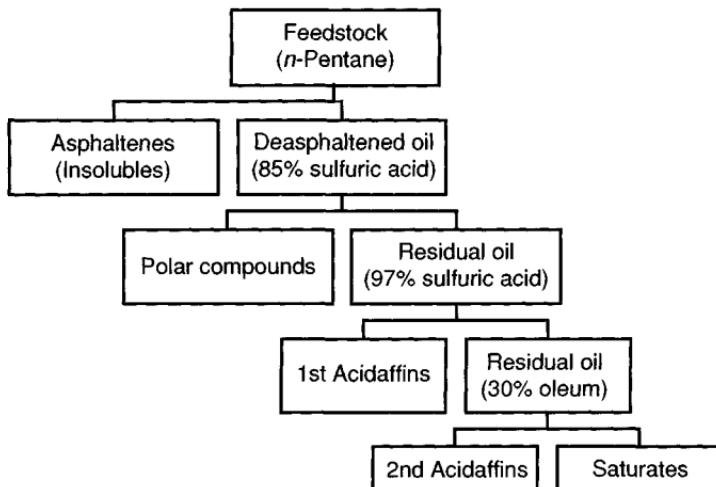


Figure 9.10. The ASTM D-2006 fractionation procedure.

often identified by the acronyms for the names: PONA (paraffins, olefins, naphthenes, and aromatics), PIONA (paraffins, *iso*-paraffins, olefins, naphthenes, and aromatics), PNA (paraffins, naphthenes, and aromatics), PINA (paraffins, *iso*-paraffins, naphthenes, and aromatics), or SARA (saturates, aromatics, resins, and asphaltenes). However, it must be recognized that the fractions produced by the use of different adsorbents will differ in content and will also be different from fractions produced by solvent separation techniques.

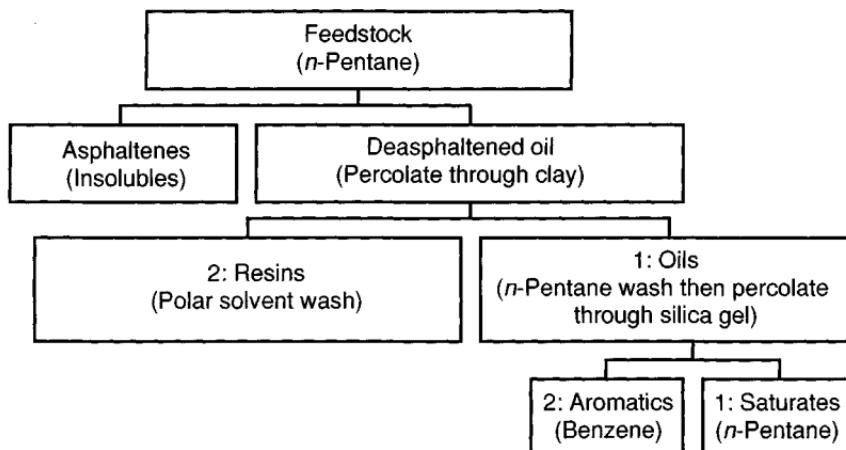


Figure 9.11. The ASTM D-2007 fractionation procedure.

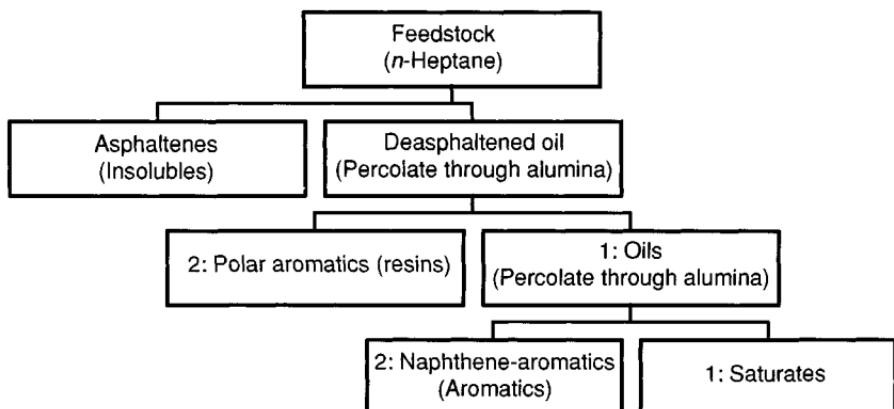


Figure 9.12. The ASTM D-4124 fractionation procedure.

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

9.4.2. Other Methods

Early investigations involved filtration of crude oils through a column of fuller's earth, and it was observed that the gasoline components appeared in the initial part of the filtrate. Subsequent investigations showed that, if light oil is drawn upward by a pump through a column of *earth*, the light aliphatic hydrocarbons accumulate in the top section. The aromatic constituents do not rise as high and the nitrogen- and sulfur-containing compounds are largely retained on the adsorbent.

A later chromatographic method involved separation into four principal fractions, asphaltenes, asphaltic resins, dark oils, and water white oils, and a fifth fraction constituting the balance of the specimen. The method consists of precipitation of asphaltenes with 40 volumes of *n*-pentane and elution of the *n*-pentane-soluble fraction from a chromatographic column of fuller's earth. The elution technique gave a series of fractions

1. *water white oils* eluted with *n*-pentane,
2. *dark oils* eluted with methylene chloride,
3. *resins* with methyl ethyl ketone, and
4. *hard resins* that were desorbed with an acetone-chloroform mixture.

The proportions of each fraction are subject to the ratio of fuller's earth to *n*-pentane-soluble materials. For example, a change in the ratio from 10:1 to 25:1 causes a decrease in the percentage of water white oils by a factor of 3:2, and the percentage of dark oils and asphaltic resins increases by about the same factor. The method, like all chromatographic procedures proposed for the fractionation of crude oils, is dominated by equilibrium conditions and does not give fractions that are different components but only blends of the same components in different proportions. Nevertheless, this method, despite this serious shortcoming, remains one of the best chromatographic methods proposed and has been used extensively as such or with some slight modification, for example, the subdivision of maltenes from crude oils into oils (*n*-pentane eluate, i.e., saturates fraction plus aromatics fractions) and resins (pyridine eluate).

Other methods of fractionation by the use of adsorbents include separation of the maltenes fraction by elution with *n*-heptane from silica gel into two fractions named aromatics and nonaromatics, which is, in fact, a separation into the two broad groups called resins and oils in other methods. The silica gel method may also be modified to produce three fractions: (1) nonaromatics eluted with *n*-heptane, (2) aromatics eluted with benzene, and (3) compounds that contain oxygen as well as sulfur and nitrogen, eluted with pyridine. Prior separation of the asphaltenes renders the procedure especially suitable and convenient for use with heavy oil and bitumen. Other modifications include successive elution with *n*-pentane, benzene, carbon tetrachloride, and ethanol.

Alumina has also been used as an adsorbent and involves (1) precipitation of asphaltenes with normal pentane, (2) elution of oils from alumina with pentane, and (3) elution of resins from alumina with a methanol-benzene mixture. In fact, the choice of the adsorbent appears to be arbitrary, as does the choice of the various solvents or solvent blend. The use of ill-defined adsorbents, such as *earths* or *clays* is a disadvantage in that certain components of the petroleum may undergo changes (for example, polymerization) caused by the catalytic nature of the adsorbent and can no longer be extracted quantitatively. Furthermore, extraction of the adsorbed components may require the use of solvents of comparatively high solvent power, such as chloroform or pyridine, which may be difficult to remove from the product fractions.

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

There are two procedures that have received considerable attention over the years and these are (1) the United States Bureau of Mines-American Petroleum

Institute (USBM-API) method and (2) the saturate-aromatic-resin-asphaltene (SARA) method. This latter method is often also called the saturate-aromatic-polar-asphaltene (SAPA) method. These two methods represent the standard methods of petroleum fractionation. Other methods are also noted, especially when the method has added further meaningful knowledge to compositional studies.

The USBM-API method (Fig. 9.8) employs ion-exchange chromatography and coordination chromatography with adsorption chromatography to separate heavy oils and residua into seven broad fractions: acids, bases, neutral nitrogen compounds, saturates, and mono-, di-, and polyaromatic compounds. The acid and base fractions are isolated by ion-exchange chromatography, the neutral nitrogen compounds by complexation chromatography using ferric chloride, and the saturates and aromatics by adsorption chromatography on activated alumina (Jewell et al., 1972a; Altgelt et al., 1979) or on a combined alumina-silica column (Hirsch et al., 1972; Jewell et al., 1972b).

The feedstock sample can be separated into chemically significant fractions that are suitable for analysis according to compound type (Jewell et al., 1972b; McKay et al., 1975). Although originally conceived for the separation of distillates, this method has been successfully applied to determination of the composition of heavy oil and bitumen (Cummins et al., 1975; McKay et al., 1976; Bunger, 1977). Originally, the method required distillation of a feedstock into narrow boiling-point fractions, but whole feedstocks, such as the bitumen from Utah or Athabasca tar sands (Selucky et al., 1977), have been separated into classes of compounds without previous distillation or removal of asphaltenes. The latter finding is supported by the separation of asphaltenes using ion-exchange materials (McKay et al., 1977; Francisco and Speight, 1984).

The SARA method (Jewell et al., 1974) is essentially an extension of the API method that allows more rapid separations by placing the two ion-exchange resins and the FeCl_3 -clay-anion-exchange resin packing into a single column. The adsorption chromatography of the nonpolar part of the same is still performed in a separation operation. Because the asphaltene content of petroleum (and synthetic fuel) feedstocks is often an important aspect of processability, an important feature of the SARA method is that the asphaltenes are separated as a group. Perhaps more important is that the method is reproducible and applicable to a large variety of the most difficult feedstocks, such as residue tar sand bitumen, shale oil, and coal liquids.

Both the USBM-API and SARA methods require some caution if the asphaltenes are first isolated as a separate fraction. For example, the asphaltene yield varies with the hydrocarbon used for the separation and with other factors (Girdler, 1965; Mitchell and Speight, 1973; Speight et al., 1984). An inconsistent separation technique can give rise to problems resulting from residual asphaltenes in the deasphaltened oil undergoing irreversible adsorption on the solid adsorbent.

The USBM-API and SARA methods are widely used separation schemes for studying the composition of heavy petroleum fractions and other fossil fuels, but several other schemes have also been used successfully and have found common usage in investigations of feedstock composition. For example, a simple alternative (Fig. 9.9) to the SARA sequence is the chromatographic preseparation of a deasphaltened sample on deactivated silica or alumina with pentane (or hexane) into saturated materials followed by elution with benzene for aromatic materials and with benzene-methanol for polar materials (resins). This allows further chromatography into narrower (more similar) fractions without mutual interference on the adsorbent.

The selection of any separation procedure depends primarily on the information desired about the feedstock. For example, separation into multiple fractions to examine the minute details of feedstock composition requires a complex sequence of steps. An example of such a separation scheme (Fig. 9.10) involves the fractionation of Athabasca tar sand bitumen into four gross fractions and subfractionation of these four fractions (Boyd and Montgomery, 1963). This allowed the investigators to study the distribution of the functional types within the bitumen.

Other investigators (Oudin, 1970) have reported that a combination chromatography using alumina and silica gel is suitable for deasphaltened oils. A more complex scheme, also involving the use of silica, resulted in the successful separation of hexane-deasphalted crude oil. There is also a report (Al-Kashab and Neumann, 1976) of the direct fractionation of hydrocarbon and heterocompounds from deasphaltened residua on a dual alumina-silica column with subsequent treatment of the polar fraction with cation- and anion-exchange resins into basic, acid, and neutral materials. The method also includes chromatography of the asphaltenes, but only with highly polar asphaltene samples are the basic and acid compounds first removed with ion-exchange resins. The remainder of the feedstock is separated into saturates, aromatics, and heterocompounds using alumina-silica adsorption. Separation of the saturates into *n*-alkanes and *iso*-alkanes plus cycloalkanes is achieved by the use of urea ($\text{H}_2\text{N.C=O.NH}_2$) and thiourea ($\text{H}_2\text{N.C=S.NH}_2$).

One of the problems of such a fractionation scheme is the initial separation of the feedstocks into two ill-defined fractions (*colloids* and *dispersant*) without first removing the asphaltenes. As already noted, asphaltenes are specifically defined by the method of separation. They are less well defined using such liquids as ethyl acetate in place of the more often used hydrocarbons, such as pentane and heptane (Speight, 1979). The use of ethyl acetate undoubtedly leads to asphaltene material in the *dispersoids* and nonasphaltene material in the *colloids*. Application of a more standard deasphalting technique would undoubtedly improve this method and provide an excellent insight into feedstock composition.

One of the common problems of any adsorption-based fractionation scheme is the nature of the adsorbent. In the early reports of petroleum fractionation (Pfeiffer,

1950), *clays* often appeared as an adsorbent to effect the separation of the feedstock into various constituent fractions. However, *clay* (fuller's earth, attapulgus clay, and the like) is often difficult to define with any degree of precision from one batch to another. Variations in the nature and properties of the clay can, and will, cause differences not only in the yields of composite fractions but also in the distribution of the compound types in those fractions. In addition, irreversible adsorption of the more polar constituent to the clay can be a serious problem when further investigations of the constituent fractions are planned.

One option for resolving this problem has been the use of more *standard* adsorbents, such as alumina and silica. These materials are easier to define and are often accompanied by guarantees of composition and type by various manufacturers. They also tend to irreversibly adsorb less of the feedstock than a clay. Once the nature of the adsorbent is guaranteed, reproducibility becomes a reality. Without reproducibility, the analytic method does not have credibility.

9.5. CHEMICAL METHODS

Methods of fractionation using chemical reactants are entirely different in nature from the methods described in the preceding sections. The basic concept of this type of separation is the step-wise production of a variety of fractions by treatment of the petroleum with the chemical reactant until fractionation is complete.

The most common methods that have been used for the separation procedure, other than the use of ferric chloride on a adsorbent (page 252), involve the use of sulfuric acid and urea adduction. Although, to be truthful, the urea adduction method is in reality a physical method, because it provides a separation that is specific to certain constituents of petroleum, it is included here. Many other methods that have been used for the chemical separation of petroleum are now included as refinery processes (Kalichevsky and Stagner, 1942; Gruse and Stevens, 1960; Speight, 1999). These acid treatments (particularly the sulfuric acid method) and the urea addition method are still widely used in the laboratory, and therefore they are included here.

9.5.1. Acid Treatment

The method of chemical separation that is commonly applied is treatment with sulfuric acid. Marcusson and Eickmann made an early reference to the use of sulfuric acid in 1908 and first precipitated the asphaltenes from asphaltic materials by treatment of the sample with low-boiling naphtha, followed by fractionation of the naphtha-soluble material with concentrated sulfuric acid (Fig. 9.13).

The precipitate produced by the sulfuric acid treatment was actually material that had been converted to an asphaltene type of product by interaction of the

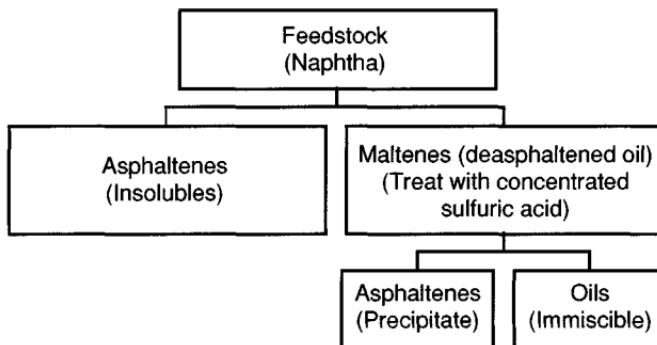


Figure 9.13. The Marcusson–Eickmann fractionation procedure.

asphaltic constituents with the sulfuric acid. It is nevertheless possible that some of the acid-precipitated material originated as asphaltenes that were incompletely precipitated by the naphtha. The constitution of the naphtha was unknown; most likely it was not pure *n*-pentane and it may even have contained hexane(s) or higher paraffins. The addition of only 20 volumes of solvent to heavy feedstocks is not a sufficient amount to completely precipitate asphaltene material.

However, the method has served as a demonstration of the type of separation that can be obtained by means of sulfuric acid. A later refinement of this principle led to the development of a technique that proposes a resolution of crude oils, crude oil residua, and asphaltic or bituminous materials into five broad fractions (ASTM D-2006) (Fig. 9.14). These fractions are distinctly different in chemical reactivity as measured by response of the fractions to cold sulfuric acid of increasing strength (sulfur trioxide concentration). The fractionation involves, like most other methods, initial separation of the sample into asphaltenes and the fraction referred to as maltenes. The fractionation of maltenes into resins and oils is often too vague for identification purposes, and the nature, or composition, of these two fractions may differ from one oil to another.

The chemical precipitation method is claimed to provide the needed subdivision of the resins and the oils to yield chemically related fractions. The names given to the individual fractions are descriptive of the steps used in the procedure. For example, the name paraffins is used for the saturated nonreactive fraction, whereas the next two groups in ascending reactivity are *second acidaffins* and *first acidaffins*. The term *second acidaffins* denotes the group of hydrocarbons having affinity for strong acid, as represented by fuming sulfuric acid. The term *first acidaffins* denotes that the constituents have an affinity for ordinary concentrated sulfuric acid. The next fraction, nitrogen bases, separated by sulfuric acid of 85% concentration, includes the most reactive components and may contain, among other components, substantially all the nitrogen-containing compounds.

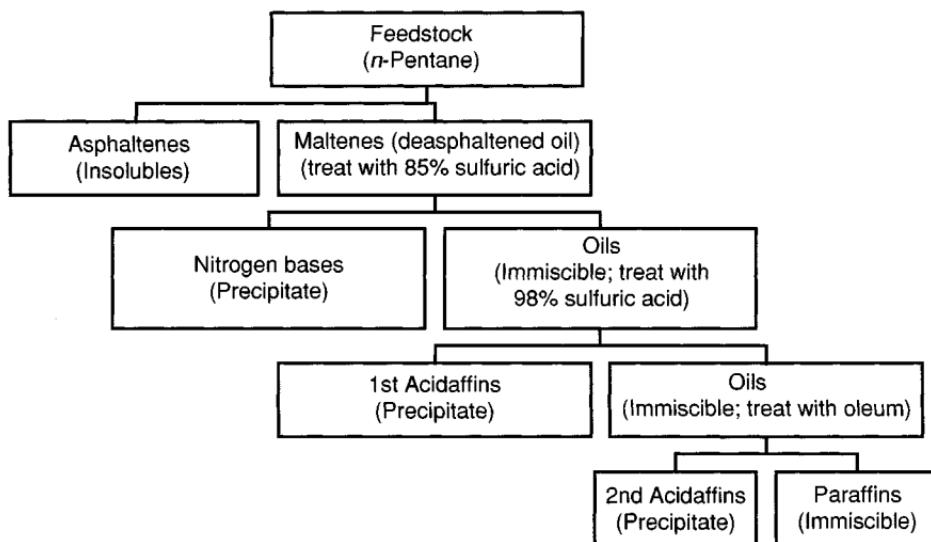


Figure 9.14. The Rostler–Sternberg fractionation procedure.

The fractionation accomplished by the sulfuric acid method is presumed to be the subdivision of crude oils or asphaltic materials into five groups of components by virtue of their chemical makeup. The method was accepted by the American Society for Testing and Materials as a standard method of test for *Characteristic Groups in Rubber Extender and Processing Oils by the Precipitation Method* (ASTM D-2006). However, there is still some doubt regarding the applicability of the method to a wide variety of petroleum, petroleum residua, and other bituminous materials (Speight, 1999), because the potential for stable emulsion formation (by sulfonation of the constituents), hence leading to difficulties in the separation procedure, is high.

There is also a relatively simple precipitation of the basic constituents of petroleum (as their hydrochlorides) by passage of dry hydrogen chloride gas through a solution of the material in a solvent such as carbon disulfide. It therefore appears that a number of refinements of the sulfuric acid method are desirable because it is apparent that not all carbonaceous liquids react in the same manner with sulfuric acid.

9.5.2. Molecular Complex Formation

The formation of crystalline molecular complexes between urea ($\text{H}_2\text{N}.\text{C}=\text{O}.\text{NH}_2$) or thiourea ($\text{H}_2\text{N}.\text{C}=\text{S}.\text{NH}_2$) and hydrocarbons has been known since the 1940s, and it is not surprising that the technique has received considerable attention with respect to its use in petroleum chemistry.

Distillation and adsorption methods of separation differentiate molecules by class and volatility (or size within any one homologous series), respectively, whereas adduct formation separates on the basis of molecular shape and, to a lesser extent, by size and class. When combined with the older fractionation methods, adduct formation can often be useful for solving separation problems, provided the limitations of the method are realized. Urea and thiourea adduction are not completely selective, as was first supposed, and there is an overlapping of structural types that adduct, especially among the higher-molecular-weight hydrocarbons.

Adduct formation may be achieved merely by bringing together the adduct former and the reagent under a wide range of reaction conditions. Preferably, the reactant is an inert hydrocarbon solvent, a reagent solvent, referred to as the activator, present in varying amounts to increase the rate of reaction, and the crystalline product that precipitates can be conveniently separated by filtration. Furthermore, the adducts may be decomposed easily, and the adducting material can be recovered by one of several procedures.

It is generally accepted that, in the urea adducts, the urea molecules are connected into spirals by hydrogen bonds between the oxygen and the amino groups of adjacent urea molecules, resulting in a channel into which the adducting compound can fit. The size of the channel limits the molecules that may adduct to those having cross-sectional dimensions equal to, or less than, those of the channel in the urea adduct; however, in certain cases, distortion of the urea lattice may occur and slightly larger molecules can adduct. The structure of the thiourea adducts is similar to that of the urea adducts. The larger size of the sulfur atom results in a channel of somewhat larger cross-sectional dimensions, hence allowing larger molecules to adduct with thiourea than are able to adduct with urea. In general, urea forms adducts with organic compounds containing a long, unbranched chain, such as the *n*-paraffins, whereas thiourea forms complexes with compounds that contain a moderate amount of branching or cyclization. However, especially among the higher-molecular-weight hydrocarbons, urea adducts can be formed from *n*-paraffins.

The relationship among structure, adductibility, and adduct stability is not as well defined for the *thiourea-adductible* compounds as for the urea-reactive hydrocarbons. The stability of any thiourea adduct is quite low, even at 0°C, and corresponds approximately to the stability of the urea completes of the lower *n*-paraffins. The high stability of the urea completes of the higher *n*-paraffins has no parallel in thiourea completes. Among the higher hydrocarbons containing a ring or branching and a long chain, there is a lesser tendency for the thiourea adducts to form than in the lower-molecular-weight homologues, as the alkyl chain apparently reduces the stability. The higher *n*-paraffins adduct fairly readily and become more stable with increasing molecular weight, but the stability of these adducts is still of the same low order of magnitude as the lower-molecular-weight *iso*-paraffins and naphthenes.

Analysis of the complexes for their mole ratio of reagent to reactant may be made by several methods. The urea (or thiourea) content of the crystalline complex may be established by nitrogen determination (Chapter 4), or the amount of organic component may be determined from carbon content (Chapter 4) or by the weight loss on dissociation of the adduct. Also, measurement of concentration changes in the reaction liquid is applicable to certain mixtures.

For urea adducts of normal hydrocarbons, the mole ratio of urea to hydrocarbon in the adduct can be represented by the equation

$$m = 0.65n + 1.5$$

where m is the mole ratio of urea to hydrocarbon and n is the number of carbon atoms in the hydrocarbon. For all practical purposes, the use of the ratio of 3.3 g of urea per gram of normal hydrocarbon is more convenient. The greater variety of hydrocarbon structures adducting with thiourea than with urea adversely affects development of an equation relating the mole ratio of thiourea to reactant. For a given number of carbon atoms, the more compact molecules are generally associated with less thiourea in the adduct than are the less compact molecules. The weight ratio decreases from 2.7 to 2.8 for aliphatic compounds and monocyclic naphthenes to 2.5 for dicyclic naphthenes and to 2.2–2.3 for condensed ring systems; the weight ratio (or unsaturated compounds) is generally very similar to that of the corresponding saturated structure.

The most practical method of decomposition of the adducts is by solution, generally with hot water. The adducted hydrocarbons form an immiscible layer on top of the aqueous urea solution and may be readily separated. Volatile reactants may be recovered by heating the adduct, either dry or with steam, and collecting the liberated hydrocarbon as it is released. Actually, a crude fractional dissociation may be accomplished in this manner or by partial solvent extraction. The least stable adduct formers are released first and may be collected. Separations of compounds from mixtures are carried out, in effect, on the basis of their stability. The most desirable results are generally obtained if all the possible material is first precipitated as the adduct; the recovered adducted material is then fractionally readducted.

In a narrow molecular weight distillation fraction containing several adductible hydrocarbon types, separation can be accomplished as a result of the difference in stability of the adducts of the different hydrocarbon homologous series. With urea, the *n*-paraffins react first, followed by the slightly branched *iso*-paraffins and by the more highly branched *iso*-paraffins and last by the cyclic structures. However, working with a wide molecular weight fraction, such as petroleum waxes, the stability of the urea adducts of lower *n*-paraffins present is of the same order of magnitude as that of the adducts of higher *iso*-paraffins and monocyclic compounds;

a mixture of types is of different molecular weights. Hence, fractional distillation of the hydrocarbon samples either before or after adduction allows better analysis of the various fractions.

Fractionation may also be effected by selective decomposition of the adduct or by selective replacement. In the former method, the adduct is extracted using a solvent of relatively poor dissociating power, whereby the least stable adducts tend to dissociate first. In selective replacement, the hydrocarbons of the less stable adducts are gradually displaced by slightly more stable adductors, and these in turn are displaced by more stable adduct formers until the most stable *n*-paraffins are employed.

The relative instabilities of the thiourea adducts renders the method less useful than the urea method. In addition, the less selective nature of thiourea adduction and the fact that large differences in stability exist within a homologous series with the urea adducts do not apply to the thiourea adducts.

Finally, the urea adduction method is not particularly amenable to tar sand bitumen because of a general lack of hydrocarbon constituents in the bitumen. The most amenable feedstock is conventional (paraffinic) petroleum, and there may be heavy oils that respond to the procedure.

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CHAPTER

10

CHROMATOGRAPHIC ANALYSIS

10.1. INTRODUCTION

The history of the use of chromatography goes back to the sixteenth century (1512) when Brunschwig, a Strasbourg surgeon, purified ethanol by a chromatographic technique. Day, an American geochemist, separated crude oils on fuller's earth (1898–1903). The major work was a systematic study carried out by Michael Tswett, a Russian botanist that is recognized as the beginning of chromatography (Meloan, 1999).

Historically, the work carried out was what we now refer to as *column chromatography*, often also referred to as *adsorption chromatography* (page 273). Many variations have been developed since the original discovery. The more common chromatographic procedures are gas chromatography, adsorption chromatography, gel permeation chromatography, ion-exchange chromatography, and high-performance chromatography, which are discussed in more detail here. Paper chromatography is used less frequently for petroleum analysis but are also included in this work (Section 10.9).

With the startling demands on the petroleum industry during and after World War II and the emergence of the age of petrochemicals and plastics, the industry needed to produce materials not even considered as products in the decade before the war. Thus the petroleum refiner took on the role of technological innovator as new and better processes were invented and advances in the use of materials for reactors were developed. In addition, it became necessary to find out more about petroleum so that refiner might be able to enjoy the luxury of predictability and plan a product slate that was based on market demand—a difficult task when the character of the crude oil was unknown! The idea that petroleum refining should be a *hit and miss* affair was not acceptable. The demand arose for a more detailed inspection of the character of petroleum. Petroleum varies markedly in properties and composition according to the source, and variations in feedstock character caused changes for optimization of existing processes as well as for the development and design of new processes.

For example, valuable information can be obtained from the *true boiling point* (TBP) curve, which is a function of percent weight distilled and temperature, that is, a boiling point distribution (Chapter 5). However, there are boiling point

limitations on this function that are well below the final boiling point (FBP) of a crude oil. In addition to the boiling point distribution, bulk physical properties such as specific gravity and viscosity have assisted in the establishment of certain empirical relationships for petroleum processing from the TBP curve. Many of these relationships include assumptions that are based on experience with a range of feedstocks. However, the movement of refining to feedstocks that contain higher proportions of coke-forming materials emphasizes the need for more definitive data that would enable more realistic predictions to be made of crude oil behavior in refinery operations.

However, regardless of the type of chromatography used for separation and identification of petroleum constituents, the mechanisms involved in the separation are basically the same. The two major mechanisms at work during a chromatographic separation are *displacement* and *partition*. Few instances involve only one mechanism, but certain types of separations emphasize one mechanism over the other.

Chromatographic procedures are often referred to as *displacement procedures*. In the simplest procedure (which relates more to the historical work), a glass column is packed tightly with powder-size dry particles, the *inert phase*. A thin layer of a sample mixture consisting of weakly adsorbed compounds and strongly adsorbed compounds is added to the top of the inert phase. A liquid, which is more strongly adsorbed to the inert phase than any of the compounds in the sample, is now poured into the top of the column. This is called the *mobile phase* and serves to wash the sample down the column, a process called *elution*.

The *inert* particles, are mainly silicates and aluminates, contain *active sites* due to *charge distribution*, and molecules of the solute attach themselves to the particles based on their relative adsorption tendencies derived from size or polarity and pass down the column as far as necessary until all of the molecules are adsorbed. An *equilibrium* is established with the strongly adsorbed molecules remaining on the column and the weakly-adsorbed molecules passing out at the bottom of the column.

The analysis of the constituents in petroleum started over 100 years ago, when in 1865 several aromatic hydrocarbons were identified as constituents of petroleum. Identification of individual constituents of petroleum continued, and the rapid advances in analytic techniques have allowed the identification of large numbers of petroleum constituents. At this time, the major chemical types of compounds that exist in crude oil have been identified and many members of the various homologous series have been separated or conclusively identified by various techniques (see Rossini et al., 1953 for historical details).

It is the purpose of this chapter to review the methods that can be used for the *identification* of the constituents of petroleum. Particular emphasis has been placed on the chromatographic techniques that have offered valuable information in the past (Altgelt and Gouw, 1975) and will continue in the future to offer valuable

information about the constituents of petroleum. Spectroscopic and spectrometric methods are not included here (unless there is some mention of use as a detector system); to emphasize the importance of spectroscopy and spectrometry, they are included as a separate chapter (Chapter 7) and their use in structural determination is described elsewhere (Chapter 11). Statistical methods, as applied to analytical chemistry, are beyond the scope of this chapter and have been omitted; the reader is referred to other, more comprehensive works on this subject (e.g., Meier and Zünd, 2000).

As elsewhere in this book, the nature of the subject matter of this chapter dictates that there is overlap with the subject matter of other chapters. This is inevitable, and the reader is referred to other relevant chapters to place the subject matter of all chapters into the proper perspective.

10.2. GAS CHROMATOGRAPHY

Gas chromatography (also referred to as *gas-liquid chromatography, GLC*) is a chromatographic method for separating the volatile components of various mixtures in which the *mobile phase* is a gas (Martin and James, 1952; Fowlis, 1995; Grob, 1995). It is, in fact, a highly efficient fractionating technique, and it is ideally suited to the quantitative analysis of mixtures when the possible components are known and the interest lies only in determining the amounts of each present. In this type of application gas chromatography has taken over much of the work previously done by the other techniques; it is now the preferred technique for the analysis of hydrocarbon gases, and gas chromatographic in-line monitors are experiencing increasing application in refinery plant control.

The longer compounds remain in a column, the more time they have to diffuse and remix. It was suggested (Martin and James, 1952) that the best separations should occur if the stationary phase was very thin and the mobile phase was changed from a liquid to a gas. This would provide fewer *foreign* molecules for the sample molecules to hit, thus reducing the mixing by diffusion. The detectors available at this time (1952) had poor response, and to separate sufficient material to be detected, a relatively thick layer of stationary phase was required. However, the liquid mobile phase could be changed to a gas. Rapid development followed.

The importance of gas-liquid chromatography lies in its powerful separating ability. Columns can have the equivalent of up to 1,000,000 theoretical plates compared with conventional distillation, which normally operates in the range of 5–10 theoretical plates.

In the case of gas-liquid chromatography (GLC or GC), the two phases are a flowing gas phase and a liquid phase held stationary on an *inert solid support*. In practice, for the older style using packed columns, a small sample (1–5 μl) is injected by means of a syringe or sample loop into a heated injection port,

where the liquid is vaporized into the flowing gas stream (usually nitrogen, helium, argon). The carrier gas transports the sample through the column (glass, copper, or stainless steel, 3- to 6-mm diameter, 1–2 m long), which is packed with a solid of large surface area. This solid support, which is commonly a diatomaceous earth or crushed firebrick, is impregnated with a *nonvolatile liquid phase*. Separation of the injected mixture occurs by partitioning between the gas stream and the liquid phase. A large number of partitions occur, and even very small differences in physical and chemical properties allow the components to become separated.

The gas stream, containing the separated compounds, then is passed through a detector. The simplest type of detector is one that measures the difference in thermal conductivity between the sample plus helium (He) or nitrogen (N_2) gas and a reference helium or nitrogen gas. The detector signal is monitored continuously by a recorder that plots the components as a function of time, resulting in gaussian shaped peaks. More recently, capillary columns, 0.05–0.53 mm in diameter and 10–100 m long, having as many as 4000 plates, are becoming common and finding use as analytical methods (ASTM D-2268).

The elapsed time between the injection and the center of a peak is called the *retention time* of that compound. Although a gas chromatograph separates compounds, the method does not identify them, but the retention time may be used as corroborating evidence in the identification of a compound by injecting a known sample under identical conditions and observing identical retention times. Another outcome of the chromatographic method is the identification of individual components of a mixture as well as the calculation of gas chromatographic *response factors* for individual compounds (ASTM D-4626). The *unknown-known comparison* then should be repeated on another column of *different polarity* to substantiate the previous agreement of retention times. Failure to use columns of different polarities to corroborate the identification of compounds can lead to embarrassing situations.

The evolution of gas chromatography has been a major factor in the successful identification of petroleum constituents. It is, however, almost impossible to apply this technique to the higher-boiling petroleum constituents because of the comparatively low volatility of these materials. It is this comparative lack of volatility in the higher-molecular-weight, asphaltic constituents of petroleum that brought about another type of identification procedure, namely, carbon-type analysis.

Thus it is not surprising that gas chromatography has been used extensively for individual component identification, as well as percentage composition, in the gaseous boiling ranges (ASTM D-2163, ASTM D-2426, ASTM D-2504, ASTM D-2505, ASTM D-2593, ASTM D-2597, ASTM D-2712, ASTM D-4424, ASTM D-4864, ASTM D-5303, ASTM D-6159, IP 264, IP 318, IP 337, IP 345), in the gasoline boiling range (e.g., ASTM D-2426, ASTM D-2427, ASTM D-3525, ASTM D-3606, ASTM D-3710, ASTM D-4420, ASTM D-4815, ASTM D-5134, ASTM D-5441, ASTM D-5443, ASTM D-5501, ASTM D-5580, ASTM D-5599,

ASTM D-5623, ASTM D-5845, ASTM D-5986, IP 425), in higher-boiling ranges such as diesel fuel (ASTM D-3524), aviation gasoline (ASTM D-3606), engine or motor oil (ASTM D-5480), and wax (ASTM D-5442), as well as in the boiling range distribution of petroleum fractions (ASTM D-2887, ASTM D-5307), light hydrocarbons in stabilized crude oil (IP 344), or the purity of solvents using capillary gas chromatography (ASTM D-2268). There are also recommendations for calibrating and checking gas chromatographic analyzers (IP 353).

Gas chromatography (GC) is the method of choice for light and middle distillates because of its high resolution. However, for high-boiling petroleum distillates, it has much more limited use because of its propensity to separate primarily by carbon number and because of the immense number of compound types and homologues in these materials, let alone their low volatility (Altgelt and Boduszynski, 1994). The two main applications here are simulated distillation (page 271) and the separation and identification of compound types and their homologues in well-defined liquid chromatographic (LC) fractions.

The technique has proved to be an exceptional and versatile instrumental tool for analyzing compounds that are of low molecular weight and that can be volatilized without decomposition. However, these constraints limit the principal applicability in petroleum science to feedstock identification when the composition is known to be in the low- to medium-boiling range. The use of this technique for direct component analysis in the heavy fractions of petroleum is not only difficult but also subject to many limitations.

For example, the number of possible components of a certain molecular weight range increases geometrically with increasing molecular weight. Furthermore, there is a corresponding sharp decrease in physical property differences between isometric structures as the molecular weight increases. Thus it is very difficult, and on occasion almost impossible, to separate and identify single components in the heavier fractions of petroleum by gas chromatography. Indeed, the molecular weights of the constituents dictate that long residence times are inevitable. This is inevitably accompanied by the requirement of increased column temperature, which decreases the residence time on the column but, at the same time, increases the possibility of thermal decomposition.

In all senses, the instrumentation for gas chromatography is fairly straightforward (Fig. 10.1). A carrier gas passes through a controller to the column (packed with an adsorbent) at the opening of which is a sample injector. The carrier gas then elutes the components of the mixture through the column to the detector, at the end of which may be another gas flow monitor.

Any gas, such as helium, argon, nitrogen, or hydrogen, that is easily distinguishable from the components in the mixture may be used as the carrier gas. Column dimensions vary, but for analytic purposes a packed column may be 6 ft (2 m) long by 3 in (6 mm) in diameter. It is also necessary to use a *dissolving* liquid as part of the column substance. This remains stationary on the adsorbent and effects

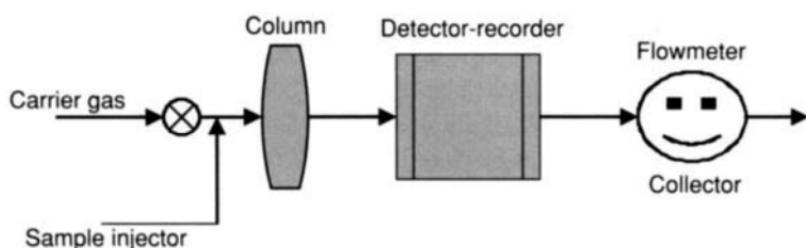


Figure 10.1. Representation of gas-liquid chromatographic equipment.

partition of the components of the mixture. The solid support is usually a porous material that allows passage of the gas. For example, kieselguhr (diatomaceous earth), which can absorb up to 40% by weight of a liquid without appearing to be overly moist, is commonly used. The supporting material should not adsorb any of the components of the mixture and must therefore be inert.

Individual components of mixtures are usually identified by their respective retention times, that is, the time required for the component to traverse the column under the specified conditions. Although tables for retention time data are available, it is more common in practice to determine the retention times of the pure compounds. The retention time of any component is itself a function of the many variables of column operation, such as the flow rate of the carrier gas and column temperature, and exact duplication of other operator's conditions may be difficult, if not impossible.

The sample size used in gas chromatography may vary upward from a microliter, and there is no theoretical upper limit to the size of the sample that may be handled if the equipment is built to accommodate it. The technique can be used for the analysis of mixtures of volatile, vaporizable compounds boiling at any temperature between absolute zero (-273°C , 459°F) and 450°C (840°F). Identification of any substance that can be heated sufficiently without decomposing to give a vapor pressure of a few millimeters of mercury is also possible.

The components of petroleum have been studied extensively by gas chromatography. This includes the determination of saturated compounds and olefins in cracked naphtha, as well as the identification of alkylbenzenes and the higher-molecular-weight normal paraffins (to at least $n\text{-C}_{40}$) in higher-boiling petroleum distillates. Previous methods usually involved the somewhat slow and careful fractional distillation followed by various analyses (physical and spectroscopic) of the fractions.

Gas chromatography can also be used to determine the three main hydrocarbon types in gasoline: saturates, olefins, and aromatics. The procedure has been used for simple characterization of gasoline and naphtha. This application demonstrates the use of two techniques, a highly selective column and a chemical reaction to

remove one group of compounds. Sometimes it is advantageous to follow such a type separation with further separations. For example, the saturate fraction after separation from aromatics and olefins can be sent to a high-efficiency column for determination of individual isomers. Determination of individual saturate isomers is difficult or impossible when olefins and aromatics are present.

Analytic distillation by gas chromatography was an important development because the demand for distillation analyses in petroleum laboratories is high. Distillation analyses by gas chromatography depend on the fact that certain non-polar silicone liquid phases elute hydrocarbons nearly in order of boiling point. The analyses are made with temperature programming, and boiling point can be correlated with elution time or with column temperature at the time of emergence. Thus a distillation curve can be constructed from gas chromatographic data. Analyses by gas chromatography usually can be as accurate as they are by precision distillation.

The use of gas chromatography for direct component analysis in the *heavier* fractions, such as residua, of petroleum is beset by many problems, not the least of which is the low volatility and high adsorption tendencies of many of the high-molecular-weight constituents of petroleum. The number of possible components in any given molecular weight range increases markedly with the molecular weight, and there is a *significant drop* in the differences in physical properties among similar structural entities. This limits the ability of gas chromatography, and unless the sample has been fractionated by other techniques to reduce the complexity, complete component analysis is difficult, if not impossible.

In view of the molecular characterizing nature of spectrometric techniques, it is not surprising that considerable attention has been given to the combined use of gas chromatography and these techniques. In recent years, the use of the mass spectrometer to monitor continuously the effluent of a chromatographic column has been reported, and considerable progress has been made in the development of rapid-scan infrared spectrometers for this purpose. The mass spectrometer, however, has the advantage that the quantity of material required for the production of a spectrum is considerably less than that necessary to produce an infrared spectrum.

The mass spectrometer identifies chemical compounds principally in terms of molecular type and molecular weight, and for many problems, therefore, it becomes necessary to use additional means of identification; the integrated gas chromatography infrared system is a very valuable complement to the mass spectrometer route.

Considerable attention has also been given to trapping devices to collect gas chromatographic fractions for examination by one or more of the spectroscopic techniques. At the same time, developments in preparative gas chromatography have contributed even more to the compositional studies of petroleum and its products. With a column size of 4- to 6-in diameter capable of dealing with sample

sizes of 200 ml or more, there is every possibility that gas chromatography will replace distillation in such areas as standard crude oil assay work.

Gas chromatography also provides a simple and convenient method for determining *n*-paraffin distribution throughout the petroleum distillate range. In this method the *n*-paraffins are first separated by activated chemical destruction of the sieve with hydrofluoric acid, and the identity of the individual paraffins is determined chromatographically. This allows *n*-paraffin distribution throughout the boiling range 170–500°C (340–930°F) to be determined.

Gas chromatography has also been found useful for the preparation of simulated distillation curves. By integrating increments of the total area of the chromatogram and relating these to the boiling points of the components within each increment, which are calculated from the known boiling points of the easily recognizable *n*-paraffins, simulated boiling point data are produced.

Gas chromatographic process analyzers have become very important in petroleum refineries. In some refineries, more samples are analyzed automatically by process chromatographs than are analyzed with laboratory instruments. These chromatographs are usually fully automatic. In some cases, after an analysis the instrument even makes automatic adjustments to the refinery unit. The chromatographs usually determine from 1 to 10 components, and the analyses are repeated at short intervals (15–20 min) over 24 h.

A more recent, very important development in gas chromatography is its combination with a mass spectrometer as the detector. The technique in which gas chromatography is combined with spectrometry (GC/MS) has proved to be a powerful tool for identifying many compounds at very low levels in a wide range of boiling matrix (ASTM D-5769) (Poirier and Das, 1984; Lin et al., 1989). By the combination of the two techniques in one instrument, the onerous trapping of fractions from the gas chromatographic column is avoided and higher sensitivities can be attained. In passing through the gas chromatographic column, the sample is separated more or less according to its boiling point.

Although insufficient component resolution is observed in most cases, the eluting compounds at any time are usually closely related to each other in boiling point and molecular weight or both and are free from interfering lower- and higher-molecular-weight species. Because of the reduced complexity of the gas chromatographic fractions, mass spectrometric scans carried out at regular intervals yield simpler spectra from which compound classes can more easily be determined.

Pyrolysis gas chromatography can be used for information on the gross composition of heavy petroleum fractions. In this technique, the sample under investigation is pyrolyzed and the products are introduced into a gas chromatography system for analysis. There has also been extensive use of pyrolysis gas chromatography by geochemists to correlate crude oil with source rock and to derive geochemical characterization parameters from oil-bearing strata.

In the technique of inverse gas chromatography, the sample under study is used as the stationary phase and a number of volatile test compounds are chromatographed on this column. The interaction coefficient determined for these compounds is a measure of certain qualities of the liquid phase. The coefficient is therefore indicative of the chemical interaction of the solute with the stationary phase. The technique has been used largely for studies of asphalt (Haines, 1971).

Despite successful applications to certain high-boiling petroleum fractions, gas chromatography itself is generally inadequate for the primary separation of such high-molecular-weight materials. Although its temperature range may well be high enough, the resolution is not sufficient for the large number of compound types and homologues in these complex materials. Resolution is further impaired by the peak broadening caused by high-molecular-weight species. For these heavy materials, liquid chromatography (LC) and supercritical fluid chromatography (SFC) are superior and are often the methods of choice. The wide choice of mobile phases for these methods permits adaptation of the methods to the compositional subtleties of the feedstocks in a manner that is not possible by gas chromatography. In addition, supercritical fluid chromatography has the additional advantage of performance with the application of pressure (Richter et al., 1998).

The primary use of gas chromatography in the analysis of heavy petroleum fractions is in simulated distillation (*simdis*) with flame ionization detection (FID) (Trestianu et al., 1985; Quimby and Sullivan, 1990; Thomson and Rynaski, 1992), in gas chromatography with atomic emission detection (Biggs et al., 1985; Biggs et al., 1987; Wylie and Quimby, 1989; Buteyn and Kosman, 1990; Kosman, 1992) and other element-specific detection (Lee et al., 1984; Arpino et al., 1987), and in combination with mass spectrometry as gas chromatography-mass spectrometry (Chapter 7).

10.3. SIMULATED DISTILLATION

Distillation is the most widely used separation process in the petroleum industry (Nelson, 1958; Speight, 1999, 2000). In fact, knowledge of the boiling range of crude feedstocks and finished products has been an essential part of the determination of feedstock quality since the start of the refining industry; the various test methods are noted elsewhere (Chapter 5). The technique has been used for control of plant and refinery processes as well as for predicting product slates. Thus it is not surprising that routine laboratory scale distillation tests have been widely used for determining the boiling ranges of crude feedstocks and a whole slate of refinery products (Chapter 5).

There are some limitations to the routine distillation tests. For example, although heavy crude oils contain volatile constituents, it is not always advisable to use distillation for identification of these volatile constituents. Thermal decomposition

of the constituents of petroleum is known to occur at approximately 350°C (660°F). However, thermal decomposition of the constituents of the heavier, but immature, crude oils has been known to commence at temperatures as low as 200°C (390°F). Thus thermal alteration of the constituents and erroneous identification of the decomposition products as *natural* constituents is always a possibility.

On the other hand, the limitations to the use of distillation as an identification technique may be economic, and detailed fractionation of the sample may also be of secondary importance. There have been attempts to combat these limitations, but it must be recognized that the general shape of a one-plate distillation curve is often adequate for making engineering calculations, correlating with other physical properties, and predicting the product slate (Nelson, 1958).

A low-resolution, temperature-programmed gas chromatographic analysis has been developed to simulate the time-consuming true boiling point distillation (ASTM D-2887). The method relies on the general observation that hydrocarbons are eluted from a nonpolar adsorbent in the order of their boiling points. The regularity of the elution order of the hydrocarbon components allows the retention times to be equated to distillation temperatures (Green et al., 1964), and the term *simulated distillation by gas chromatography* (or simdis) is used throughout the industry to refer to this technique (Altgelt and Boduszynski, 1994).

The method has been well researched in terms of method development and application (Hickerson, 1975; Green, 1976; Stuckey, 1978; Vercier and Mouton, 1979; Thomas et al., 1983; Romanowski and Thomas, 1985; MacAllister and DeRuiter, 1985; Schwartz et al., 1987; Thomas et al., 1987). The benefits of the technique include good comparisons with other ASTM distillation data as well as application to higher-boiling fractions of petroleum. This offers a valuable aid to process control operations and product testing. In fact, since the introduction of ASTM D-2887, the method has gained widespread acceptance by process chemists and process engineers for plant operation control.

The full development of simulated distillation as a routine procedure has been made possible by the massive expansion in gas chromatographic instrumentation (such as the introduction of automatic temperature programming) since the 1960s. In fact, a fully automated simulated distillation system, under computer control, can operate continuously to provide finished reports in a choice of formats that agree well with true boiling point data. For example, data output includes the provision of the corresponding Engler profile (ASTM D-86) as well as the prediction of other properties, such as vapor pressure and flash point (DeBruine and Ellison, 1973).

Simulated distillation by gas chromatography is applied in the petrochemical industry to obtain true boiling point distributions of distillates and crude oils (Butler, 1979). Two standardized methods, ASTM D-2887 and D-3710, are available for the boiling point determination of petroleum fractions and gasoline, respectively. The ASTM D-2887 method 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 ASTM D-2887 methods for higher-boiling petroleum materials to 800°C (1470°F) atmospheric equivalent boiling point (Schwartz et al., 1988).

Interestingly, simdis techniques not only have upper temperature limits but also lower limits. In gas chromatography-simdis, the lower limit is determined by the resolution of the solvent peak from the first eluting sample peak. For this reason, the ASTM method D 2887 is restricted to samples of initial boiling points of at least 38°C (100°F). In the supercritical fluid chromatography method, the lower boiling limit is dependent on the initial column temperature and pressure. The lowest possible pressure of carbon dioxide (CO₂) is about 800 psi, namely, the vapor pressure in the supply cylinder at room temperature. However, for many high-boiling samples lacking low-boiling components, a higher initial pressure, e.g., 850 psi, avoids unnecessarily long analysis times while providing the desirable resolution of the lower members. This restricts the lower boiling temperature of samples to be analyzed by supercritical fluid chromatography to about 120°C (250°F).

This simdis procedure is particularly adaptable to the simulated distillation of heavy oil and bitumen and samples that contain large amounts of nonvolatile residue. The procedure may also be applied to heavy gas oil samples that have a final boiling point in excess of 525°C (975°F).

For the simulated distillation of heavy oil and bitumen, two chromatographic analyses are performed to characterize the sample. The volatile components of the sample are analyzed by a standard simulated distillation procedure, and a separate assay is performed to determine the amount of volatile material in the sample by an internal standard technique. The data from the simulated distillation is then corrected for the nonvolatile residue, and results are reported as percentages of the total sample.

10.4. ADSORPTION CHROMATOGRAPHY

When chemists refer to *adsorption chromatography* or to *column chromatography*, they usually mean a glass column with a mobile phase passing through the *inert phase* (Table 10.1) by the force of gravity, mild suction, or at most a few pounds of pressure. The column may or may not be equipped with an attached solvent reservoir for the *mobile phase* (Table 10.2) but does not have an attached stopcock to control the flow rate and should be wide bore to prevent plugging with viscous mobile phases. Removable bottoms are used for those separations that require long times. The bottom can be removed and the column packing pushed out with a plunger. The column packing then can be

Table 10.1. Materials Used as Stationary Phases for Adsorption Chromatography

Fuller's earth	Most active
Charcoal	
Activated alumina	
Magnesium silicate	
Silica gel	
Calcium oxide	
Magnesium oxide	
Calcium carbonate	
Calcium phosphate	
Calcium carbonate	
Potassium carbonate	
Sodium carbonate	
Talc	
Starch	
Sugar(s)	Least active

sectioned and the desired compounds extracted or washed from the inert phase for further use.

Adsorption chromatography has helped to characterize the group composition of crude oils and hydrocarbon products since the beginning of the twentieth century (Chapter 10) (Altgelt and Guow, 1979; Altgelt and Boduszynski, 1994; Masel, 1995). In fact, it is probably the most used and abused of all of the

Table 10.2. Solvents Used as Mobile Phases for Adsorption Chromatography

Petroleum ether/petroleum naphtha	Least interference with adsorbent
Carbon tetrachloride	
Cyclohexane	
Carbon disulfide	
Ether	
Acetone	
Benzene or toluene	
Esters	
Chloroform and other chloro-solvents	
Alcohols	
Pyridine	
Organic acids	
Various mixtures of the above solvents	
Pyridine/water	Most interference with adsorbent

chromatographic methods that have been applied to petroleum characterization! The analytical chemist must choose and rationalize the number of fractions that are to be the outcome of the separation procedure, and this rationalization must be based on the manner in which the data will be used. The techniques used to produce fractions that will be used for process predictability should be approached differently from the techniques used to search for geochemical markers. The advisability of separating petroleum, heavy oil, and bitumen into a multitude of fractions must be given serious preapplication consideration. The analytical chemist must ask himself/herself, and be prepared to advise the process chemist or process engineer, about the number of fractions necessary to accomplish the goal. Four fractions might suffice, thus the tendency to proceed and separate the feedstock into twenty or more discrete fractions is always a dream! Such temptation must be avoided, and fractionation schemes that are meaningful to the task are to be preferred.

The apparatus for the various chromatographic separation schemes usually consists of a glass column 1–5 cm in diameter and 20–100 cm long, packed with a solid material (called the inert phase, although it seldom is inert) such as silica gel or diatomaceous earth (ASTM D-2007). The sample is placed as a thin band on top of the packing and washed down the column with a liquid (mobile phase). As the compounds move down the column, small differences in their molecular shape and polarity allow them to become separated.

The method can be applied to conventional petroleum, heavy oils, residua, and bitumen, but subtle differences may be applied to the procedure depending on the nature of the material to be separated. For example, when conventional petroleum is to be separated, the feedstock may first be topped (the volatile constituents removed) before separation. The procedure separates the feedstock into *saturate, aromatic, resin, and asphaltene fractions* or specific chemical types such as petroleum sulfonates (ASTM D-3712).

In general, the method involves deasphalting the feedstock (Chapter 9), and the resulting deasphalted oil is passed through or refluxed on a recycle adsorption apparatus packed with Attapulgus clay (Fig. 10.2). Resins adsorb on the Attapulgus clay, whereas the saturates and aromatics are carried to the kettle. The resins are eluted from the Attapulgus clay with methyl ethyl ketone and tetrahydrofuran containing 50% water by volume. Separation of the saturates and aromatics is performed on a chromatographic column packed with alumina and silica gel. The saturates and aromatics are eluted with *n*-pentane and benzene, respectively. Any resin constituents that may have remained are eluted with methyl ethyl ketone. All fractions are determined gravimetrically after evaporation of the solvent.

The fractions denoted as saturates, aromatics, resins, and asphaltenes in this procedure are defined operationally by the specific test conditions described in the method and separations according to molecular type. Instead, the fractions represent a separation based on solubility and strength of adsorption and must

be identified with the procedure by which they are generated. This operational definition of the fractions is emphasized because similar terminology for designating fractions is used by methods using different separation conditions.

In practice, the separation is reproducible and hence useful for evaluating similarities and differences among different feedstock samples.

One of the common problems of such a fractionation scheme is the nature of the adsorbent. In the early reports on petroleum fractionation, *clay* often appeared as an adsorbent to effect separation of the feedstock into various constituent fractions. However, clay (*fuller's earth*, *attapulgus clay*, *attapulgite*, and the like) is often difficult to define with any degree of precision from one batch to another. Variations in the nature and properties of the clay can, and will, cause differences not only in the yields of composite fractions but also in the distribution of the compound types in those fractions. In addition, irreversible adsorption of the more polar constituents on the clay can be a serious problem when further investigations of the constituent fractions are planned.

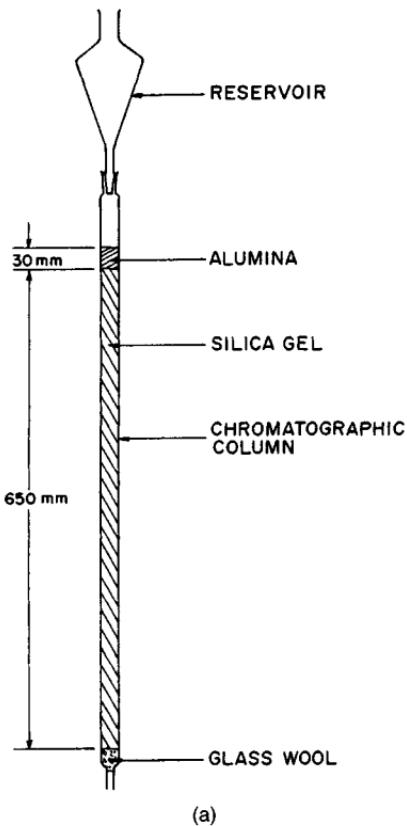


Figure 10.2. Adsorption chromatography using (a) a standard column and (b) a recycle apparatus.

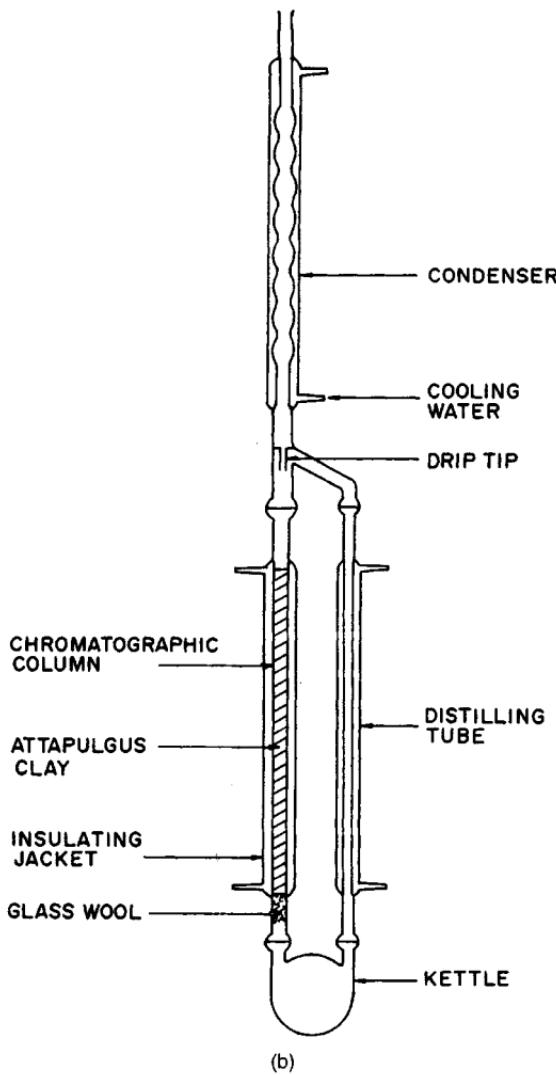


Figure 10.2. (Continued)

One option for resolving this problem has been to use more *standard adsorbents* such as alumina and silica. These materials are easier to define and are often accompanied by guarantees of composition and type by various manufacturers. They also tend to adsorb less of the feedstock than a clay. Once the nature of the adsorbent is guaranteed, reproducibility becomes a reality. Without reproducibility the analytical method does not have credibility.

The type and relative amount of certain hydrocarbon classes in the matrix can have a profound effect on the quality and performance of the hydrocarbon product.

The fluorescent indicator adsorption (FIA) method (ASTM D-1319) has served for over 30 years as the official method of the petroleum industry for measuring the paraffinic, olefinic, and aromatic content of gasoline and jet fuel. The technique consists of displacing a sample under *iso*-propanol pressure through a column packed with silica gel in the presence of fluorescent indicators specific to each hydrocarbon family. Despite its widespread use, FIA has numerous limitations (Suatoni and Garber, 1975; Miller et al., 1983; Norris and Rawdon, 1984).

The segregation of individual components from a mixture can be achieved by application of adsorption chromatography in which the adsorbent is either packed in an open tube (column chromatography) (Altgelt and Guow, 1979) or shaped in the form of a sheet (thin-layer chromatography, TLC) (Sharma et al., 1998). A suitable solvent is used to elute from the bed of the adsorbent. Chromatographic separations are usually performed for the purpose of determining the composition of a sample (Snyder, 1968). Even with such complex samples as petroleum, much information about the chemical behavior of a fraction can be gained from the separation data (Chapter 15).

In the present context, the challenge is the nature of the heteroatomic species in the heavier feedstocks. It is these constituents that are largely responsible for coke formation and catalyst deactivation during refining operations. Therefore, it is these constituents that are the focus of much of the study. An ideal integrated separation scheme for the analysis of the heteroatomic constituents should therefore meet several criteria:

The various compound types should be concentrated into a reasonable number of discrete fractions, and each fraction should contain specific types of the heteroatomic compounds. It is also necessary that most of the heterocompounds be separated from the hydrocarbons and sulfur compounds that may constitute the bulk of the sample.

Perhaps most important, the separation should be reproducible such that the yields of the various fractions and the distribution of the compound types among the fractions should be constant within the limits of experimental error.

The separation scheme should be applicable to high-boiling distillates and heavy feedstocks such as residua because heteroatomic compounds often predominate in these feedstocks.

The separation procedures should be relatively simple to perform and free of complexity.

Finally, the overall separation procedure should yield quantitative or, at worst, near quantitative recovery of the various heteroatomic species present in the feedstock. There should be no significant loss of these species to the adsorbent or, perhaps more important, any chemical alteration of these compounds. Should chemical alteration occur, it will give misleading data

that have could serious effects on refining predictions or on geochemical observations.

Group type analysis by means of chromatography has been applied to a wide variety of petroleum types and products. These types of analysis are often abbreviated by the names PONA (paraffins, olefins, naphthenes, and aromatics), PIONA (paraffins, *iso*-paraffins, olefins, naphthenes, and aromatics), PNA (paraffins, naphthenes, and aromatics), PINA (paraffins, *iso*-paraffins, naphthenes, and aromatics), or SARA (saturates, aromatics, resins, and asphaltenes).

The US Bureau of Mines-American Petroleum Institute (USBM-API) method allows fractionation of petroleum samples into acids, bases, neutral nitrogen compounds, saturates, and mono-, di-, and polynuclear aromatic compounds. Multidimensional techniques, that is, the combination of two or more chromatographic techniques, can be very useful to gain further information about the individual components of chemical groups. Compounds can be isolated and identified from complex matrices, and detailed *fingerprinting* of petroleum constituents is feasible (Altgelt and Gouw, 1975).

In normal phase chromatography (see above), the mobile phase is nonpolar and the column packing is polar in nature. Separation occurs because sample molecules dissolved in the mobile phase interact with the packing. The molecules are temporarily adsorbed and, after some time, returned to the mobile phase. This process of adsorption-desorption occurs many times for a molecule on its way through the column. The greater the compound's polarity, the more strongly it interacts with the sorbent surface, the more it is retained, and the later it elutes various types of interaction occur, from a weak induced dipole-induced dipole interaction (London forces) to hydrogen bonding to strong acid-base attraction.

Normal phase partitioning chromatography is a variant of normal phase chromatography. Here the column packing is coated with a layer of polar liquid that is immiscible with the nonpolar mobile phase and remains on the packing as the stationary phase. Sample molecules move back and forth between the two phases and are partitioned between these according to their respective solubility in the phases. Polar sample molecules ordinarily have a greater solubility ratio in favor of the stationary phase than less polar ones and spend more time there. Consequently, they elute later than nonpolar molecules. During the last two decades, so-called bonded phases have replaced the liquid stationary phases in partitioning chromatography.

Bonded phase packings are usually silica particles with chemically modified surfaces. The hydroxyl (OH) groups on the silica are either silanized or esterified and, in effect, replaced by organic groups, mostly paraffinic hydrocarbons of eight or more carbon atoms. These hydrocarbons are nonpolar and offer no advantage in normal phase chromatography. However, they are very useful in reversed-phase chromatography, where the sample is eluted with a very polar solvent such as acetonitrile and even mixtures of acetonitrile or similar solvents with methanol or

water. Here the sample molecules can partition again between a polar phase and a nonpolar one, except that the phases are reversed from those in normal phase chromatography. Here, the nonpolar molecules are more soluble in the stationary phase than in the polar mobile phase and are, therefore, retained more strongly than polar molecules.

The advantage of *reversed-phase chromatography* with its combination of an inert packing surface and a polar mobile phase is that, theoretically at least, it is a very mild method and prevents sample loss due to irreversible adsorption of highly polar molecules, which can be a serious problem in normal phase chromatography of high-boiling petroleum fractions. Unfortunately, it is difficult to completely cover the silica surface with the organic phase. Often a small percentage of the silica hydroxyl groups remains unreacted and is available for interaction with polar sample molecules that may then be strongly adsorbed.

Fractionation of aromatics by ring number is best done on column packings with bonded phases, for example, amino-, cyano-, phenyl-, or nitro-derivatized silica (Altgelt and Boduszynski, 1994). Separation on these packings proceeds only nominally by ring number, but the method really discriminates by the number of pi electrons or double bonds in the ring system. For cata-condensed aromatics, this is equivalent to ring number separation. However, peri-condensed molecules have fewer double bonds than cata-condensed molecules with the same ring number. For instance, pyrene (4 rings, 8 double bonds) elutes after phenanthrene (3 rings, 7 double bonds) and before chrysene (4 rings, 9 double bonds).

Molecules with nonplanar aromatic ring systems, usually sterically hindered, elute before planar ones and long, stretched-out polynuclear aromatic systems elute later than more compact ones. Generally, molecules with a larger (aromatic) surface area can interact with more polar groups on the packing surface and will, therefore, be more strongly retained.

An extension of adsorption chromatography, *ligand exchange chromatography* (LEC) has been used as a way to separate sulfur compounds from hydrocarbons. The method exploits the specific interactions of sulfur compounds—or other heteroatoms—with specific metal ions. Silver, mercury, copper, and zinc ions, for example, form coordination complexes with (aliphatic) sulfides, whereas palladium ions interact strongly with (aromatic) thiophenic compounds. These metals, deposited as chlorides or other salts on silica, can therefore selectively slow down the elution of sulfur compounds relative to hydrocarbons on a chromatographic column (Nishioka et al., 1986a, 1986b, 1986c, 1986d).

10.5. GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (also referred to as *size exclusion chromatography* and on occasion as *gel filtration chromatography*) is a chromatographic technique

in which the separation is based on differences in the size of the sample molecules. The column packing is made from *beads* of a porous gel which separate according to molecular size.

Large molecules cannot fit into the gel at all and are washed out of the column. The lowest-molecular-weight molecule that does not enter the gel is called the *exclusion limit*, and the volume required to elute the large molecules is called the *void volume*. The smaller molecules can permeate the gel; the smaller the molecule, the farther the penetration and the greater the retardation on or within the gel. This results in a separation because it requires more solvent to wash the smaller molecules out of the gel.

The size of the pores determines the molecular weight range of the compounds that can be separated. Size exclusion is often used to clean up an extracted solution such as removing waxes from the residua that are produced in a variety of methods.

A general rule is that *compounds that differ by 10% in size can be separated in the same column*. A series of columns, each fitted with a different exclusion limit gel, can be used to separate a multicomponent mixture.

Gel filtration chromatography (GFC), has been successfully applied to aqueous systems by biochemists for more than three decades (Porath and Flodin, 1959). This technique was developed using soft, cross-linked dextran beads. The other technique, gel permeation chromatography (GPC, also called size exclusion chromatography, SEC), uses semirigid, cross-linked polystyrene beads (Moore, 1964). In either technique, the packing particles swell in the chromatographic solvent and form a porous gel structure.

The distinction between the methods is based on the degree of swelling of the packing; the dextran swells to a much greater extent than the polystyrene. Subsequent developments of rigid porous packings of glass, silica, and silica gel have led to their use and classification as packings for gel permeation chromatography.

Gel permeation chromatography, or called size exclusion chromatography, in its simplest representation consists of column(s) packed with gels of varying pore sizes in a liquid chromatograph (Fig. 10.3) (Otacka, 1973). Under conditions of constant flow, the solutes are injected onto the top of the column, whereupon they appear at the detector in order of decreasing molecular weight. The separation is based on the fact that the larger solute molecules cannot be accommodated within the pore systems of the gel beads and thus are eluted first. On the other hand, the smaller solute molecules have increasing volume within the beads, depending on their relative size, and require more time to elute (Fig. 10.4).

Thus it is possible, with careful flow control, calibration, injection, and detection (usually by refractive index or UV absorption), to obtain an accurate chromatographic representation of the molecular weight distribution of the solute (Gillyon, 1981). This must of course assume that there is no chemical or physical interaction between the solute and the gel that negates the concept of solute size and pore size.

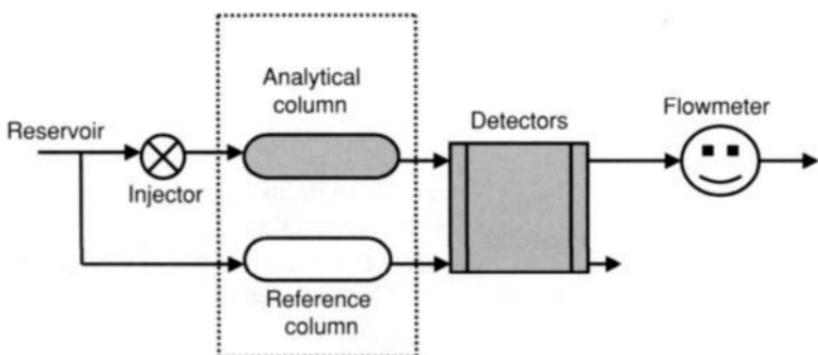


Figure 10.3. Representation of gel permeation chromatographic equipment.

For example, highly polar small molecules that could associate in solution and are difficult to dissociate could conceivably appear in the *incorrect* molecular weight range.

In theory, gel permeation chromatography is an attractive technique for the determination of the number average molecular weight (M_n) distribution of petroleum fractions. However, it is imperative to recognize that petroleum contains constituents of widely differing polarity, including nonpolar paraffins and naphthenes (acyclic compounds), moderately polar aromatics (mononuclear and condensed),

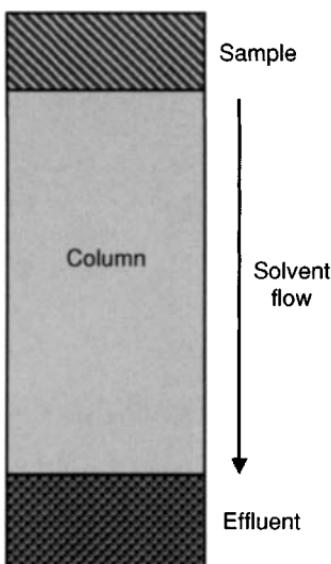


Figure 10.4. Representation of the separation by gel permeation chromatography.

and polar nitrogen, oxygen, and sulfur species. Each particular compound type interacts with the gel surface to a different degree. The strength of the interaction increases with increasing polarity of the constituents and with decreasing polarity of the solvent. It must therefore be anticipated that the ideal linear relationship of $\log M_n$ against elution volume V_e that may be operative for nonpolar hydrocarbon species cannot be expected to remain in operation. It must also be recognized that the lack of realistic standards of known M_n distribution and of chemical nature similar to that of the constituents of petroleum for calibration purposes may also be an issue. However, gel permeation chromatography has been used in the study of petroleum constituents, especially the heavier constituents, and has yielded valuable data (Oelert, 1969; Weber and Oelert, 1971; Albaugh et al., 1971; Reerink and Lijzenga, 1975; Ferguson and O'Brien, 1981; Aaberg and Tjessem, 1982; Baltus and Anderson, 1984; Guieze and Williams, 1984; Sanchez et al., 1984; Hausler, 1985; Hausler and Carlson, 1985; Reynolds and Biggs, 1988).

The adoption of gel permeation chromatography represents a novel approach to the identification of the constituents because the method is not limited by the vapor pressure of the constituents. However, the situation is different with heavy petroleum samples. These are not homologous mixtures differing only in molecular weight. In any particular crude oil a large variety of molecular species, varying from paraffinic molecules to the polynuclear aromatic ring systems, may not follow the assumed physical relationships that the method dictates from use with polymers (Altgelt, 1968, 1970).

Size exclusion chromatography is the separation method that comes closest to differentiating by molecular weight only and is almost unaffected by chemical composition. The method actually separates by molecular size and has been used to measure molecular weights (Altgelt and Guow, 1979; Hagel and Janson, 1992), although there is some question about the value of the data when the method is applied to asphaltenes (Speight et al., 1985).

Size exclusion chromatography is usually practiced with refractive index detection and yields a mass profile (concentration vs. time or elution volume) that can be converted to a mass vs. molecular weight plot by means of a calibration curve. The combination of size exclusion chromatography with element specific detection has widened this concept to provide the distribution of heterocompounds in the sample as a function of elution volume and molecular weight.

The use of size exclusion chromatography with reverse phase high-performance liquid chromatography (HPLC) with a graphite furnace atomic absorption (GFAA) detector has been described for measuring the distribution of vanadium and nickel in high-molecular-weight petroleum fractions, including the asphaltene fraction (Fish and Komlenic, 1984; Fish et al., 1984; Sarowha et al., 1996; Varotsis et al., 1998). With the use of variants of this technique, inductively coupled and direct-current plasma atomic emission spectroscopy (ICP and DCP), the method was

extended and the former size exclusion chromatography-graphite furnace atomic absorption (SEC-GFAA) method was improved (Biggs et al., 1985, 1987), allowing the separation to be continuously monitored.

The combination of gel permeation chromatography with another separation technique also allows the fractionation of a sample separately by molecular weight and by chemical structure. This is particularly advantageous for the characterization of the heavier fractions of petroleum materials because there are limitations to the use of other methods (Altgelt, 1965, 1968, 1970). Thus it is possible to obtain a matrix of fractions differing in molecular weight and in chemical structure. It is also considered advisable to first fractionate a feedstock by gel permeation chromatography to avoid overlap of the functionality that might occur in different molecular weight species in the separation by other chromatographic methods.

In short, the gel permeation chromatographic technique concentrates all of a specific functional type into one fraction, with the recognition that there will be a wide range of molecular weight species in that fraction. This is especially true when the chromatographic feedstock is a whole feed rather than a distillate fraction.

10.6. ION-EXCHANGE CHROMATOGRAPHY

Ion exchange is a process in which one type of ion in a compound is exchanged for a different type, cation for cation and anion for anion. For example, calcium, iron, and magnesium ions can be removed from water by being exchanged for sodium ion.

Ion-exchange chromatography is an ion exchange process in which the desired ions are exchanged in sequence and are eluted from a column much the same as compounds are eluted from a column in column chromatography.

Ion chromatography is the same as ion exchange chromatography, except that it includes a provision for removing the ions in the eluting agent, so that sensitive electrochemical detection is possible. The equipment used in ion-exchange chromatography is similar to that used in column chromatography and can be identical for most separations.

An interesting historical aside to the use of ion-exchange chromatography occurs in the biblical account of Moses at Marah (Christian Bible, Exodus, Chapter 15, Verses 23–25; see also Christian Bible, Numbers, Chapter 33, Verses 8–9), one of the stations of the exodus where the Israelites found bitter water. Moses reputedly:

was shown a tree which, when he had cast it into the water, the waters were made sweet.

Marah actually means “bitter” and the explanation is that the oxidized cellulose exchanged with the salt ions that gave the water its peculiar taste. Whether or not

this is true can be questioned but what does matter is that the people of those times were aware of such effects!

Other records as far back as Aristotle (384–322 B.C.E.) indicate that soils and sand filters were used to treat impure drinking water. Sir Roger Bacon (1561–1626), an English philosopher, observed in the early 1600s that:

salt water passed through earth through 10 vessels, one within another, and yet it hath not lost its saltiness as to become potable, but when drayned through 20 vessels hath become fresh.

The first systematic studies were made to determine why ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ and potassium chloride (KCl) did not wash out of soil (Thompson, 1850; Way, 1850). It was observed that if these compounds were passed through a column of soil, calcium sulfate (CaSO_4) and calcium chloride (CaCl_2) would be obtained in the filtrate. Two years later (Way, 1852), systematic studies of the process were commenced and the term *base exchange* was derived because of the basic character of the exchanged elements.

Ion-exchange chromatography is widely used in the analyses of petroleum fractions for the isolation and preliminary separation of acid and basic components. This technique has the advantage of greatly improving the quality of a complex operation, but it can be a very time-consuming separation.

Ion-exchange resins are prepared from aluminum silicates, synthetic resins, and polysaccharides. The most widely used resins have a skeletal structure of polystyrene cross-linked with varying amounts of divinylbenzene. They have a loose gel structure of cross-linked polymer chains through which the sample ions must diffuse to reach most of the exchange sites. Because ion-exchange resins are usually prepared as beads that are several hundred micrometers in diameter, most of the exchange sites are located at points quite distant from the surface. Because of the polyelectrolytic nature of these organic resins, they can absorb large amounts of water or solvents and swell to volumes considerably larger than the dried gel. The size of the species that can diffuse through the particle is determined by the intermolecular spacing between the polymeric chains of the three-dimensional polyelectrolyte resin.

Although ion-exchange resins have a wide use, the major issue in the petroleum industry is with *nonaqueous* chromatography on ion-exchange resins. The technique has found widespread use in fractionating petroleum into fractions that are comprised of various functional types. Thus acidic and basic components can be separated from heavy petroleum fractions.

Before a separation procedure is initiated, a column must be flushed with four void volumes of mobile phase to mitigate *bleeding*. The sample, dissolved at about 20 wt% concentration in the appropriate solvent, is introduced into a pair of columns connected in series, usually with the anion column first and the cation

column second. The *neutral fraction* is eluted at 40°C (104°F) with 2.5 times the void volume of solvent.

After elution, the resins are transferred from the columns to a Soxhlet apparatus. The acids are extracted from the anion-exchange resins with a benzene-formic acid azeotrope and the bases from the cation-exchange resins with benzene plus propylamine. The amine must be added slowly, in contrast to the formic acid. Modifications of resin preparation and elution and extraction conditions allow the separation and isolation of neutrals, weak and strong acids, and weak and strong bases (Green et al., 1984).

The technique is complex and tedious. The preparation and conditioning of the resins is critical for their stability as well as for their performance. Bleeding (i.e., the release of decomposition products from the ion-exchange resins) may be an issue (Strachan and Johns, 1987). The amphoteric character of certain compounds, which causes them to be classified either as acids or as bases, depending on the sequence of the ion-exchange resins the sample has to pass, must also be given consideration. With anion-exchange resins first, the amphoteric species are collected as part of the acid fraction, but with cation-exchange resins first, they are collected as part of the base fraction. By performing the analysis both ways, the amount of amphoteric material can be measured. In fact, the correct sequence of ion exchange columns allows the amphoteric species fraction to be collected as a distinct and separate fraction.

Ion-exchange chromatography procedures often advocate use of the whole feedstock rather than use of deasphaltened oil thereby foregoing the precipitation of asphaltenes as a first step in the separation of the feedstock.

The technique can also be used for the separation and isolation of nitrogen compounds from crude oil fractions. This gives fractions that are, chemically, much better defined as concentrates of acids and one or several concentrates of bases. Neutral heterocompounds can also be isolated by charge-transfer chromatography on Attapulgus clay coated with ferric chloride (FeCl_3), and hydrocarbon species can be subdivided into saturates and aromatics in a separate column.

For example, cation-exchange chromatography has been used successfully to isolate the nitrogen constituents in a petroleum fraction (Snyder and Buell, 1965; Drushel and Sommers, 1966; McKay et al., 1974). The relative importance of these compounds in petroleum has arisen because of their deleterious effects in many petroleum refining processes. They reduce the activity of cracking and hydrocracking catalysts and contribute to gum formation, color, odor, and poor storage properties of the fuel. However, not all basic compounds isolated by cation-exchange chromatography are nitrogen compounds (Okuno et al., 1967). Anion-exchange chromatography is used to isolate the acid components (such as carboxylic acids and phenols) from petroleum fractions.

If no subdivision of the polar species into acid and base fractions is desired, much simpler methods can be used for the separation of feedstock fractions into saturates, aromatics, and polars (Section 10.4).

10.7. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

High-performance liquid chromatography (HPLC) (Fig. 10.5), particularly in the normal phase mode, has found great utility in separating different hydrocarbon group types and identifying specific constituent types (IP 343, IP 391, IP 424, IP 436) (Colin and Vion, 1983; Miller et al., 1983; Petryka, 1983; Chartier et al., 1986).

Of particular interest is the application of the high-performance liquid chromatography technique to the identification of the molecular types in nonvolatile feedstocks such as residua, and the molecular species in the asphaltene fraction have been of considerable interest (Chmielowiec et al., 1980; Alfredson, 1981; Bollet et al., 1981; Colin and Vion, 1983; George and Beshai, 1983; Felix et al., 1985; Coulombe and Sawatzky, 1986; Speight, 1986).

However, a severe shortcoming of most high-performance liquid chromatographic approaches to a hydrocarbon group type of analysis is the difficulty in obtaining accurate response factors applicable to different distillate products. Unfortunately, accuracy can be compromised when these response factors are used to analyze hydrotreated and hydrocracked materials having the same boiling range. In fact, significant changes in the hydrocarbon distribution within a certain group type cause the analytical results to be misleading for such samples because of the variation in response with carbon number exhibited by most routinely used HPLC detectors (Drushel, 1983).

Several recent high-performance liquid chromatographic separation schemes are particularly interesting because they also incorporate detectors not usually associated with conventional hydrocarbon group types of analyses (Matsushita

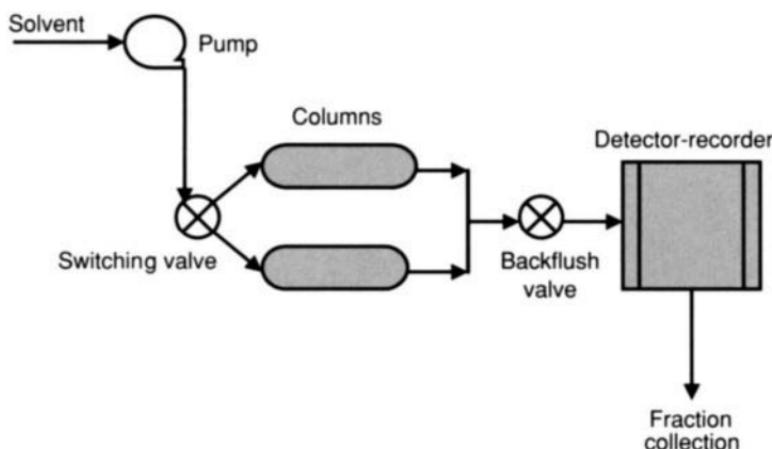


Figure 10.5. Representation of high-performance liquid chromatographic equipment.

et al., 1981; Miller et al., 1983; Norris and Rawdon, 1984; Rawdon, 1984; Lundanes and Greibokk, 1985; Schwartz and Brownlee, 1986). The ideal detector for a truly versatile and accurate hydrocarbon group type of analysis is one that is sensitive to hydrocarbons but demonstrates a response independent of carbon number. More recent work (Hayes and Anderson, 1985, 1986, 1987) has demonstrated the merits of the dielectric constant detector as an integral part of a hydrocarbon group analyzer system.

In general, the amount of information that can be derived from any chromatographic separation, however effective the separation, depends on the detectors (Hayes and Anderson, 1986; Pearson and Gharfeh, 1986). As the field of application for high-performance liquid chromatography has increased, the limitations of commercially available conventional detectors such as ultraviolet/visible absorption (UV/VIS) and refractive index (RI) have become increasingly restrictive to the growth of the technique. This has led a search for detectors capable of producing even more information. The so-called hyphenated techniques are the outcome of this search.

The general advantages of the high-performance liquid chromatography method are (1) each sample is analyzed *as received*; (2) the boiling range of the sample is generally immaterial; (3) the total time per analysis is usually of the order of minutes; and (4) the method can be adapted for on-stream analysis.

10.8. SUPERCRITICAL FLUID CHROMATOGRAPHY

A supercritical fluid is defined as a substance above its critical temperature that has properties not usually found at ambient temperatures and pressures. Use of a fluid under supercritical conditions conveys to the fluid extraction capabilities that allow the opportunity to improve recovery of a solute (Taylor, 1996).

Thus supercritical fluid chromatography (SFC) combines the advantages of gas and liquid chromatography in that its mobile phase has the low viscosity of a gas and the variable solvent strength of liquids. Under the simplest conditions (constant pressure, only 1 mobile phase), supercritical fluid chromatography has nearly the resolution of gas chromatography, but its performance can be further enhanced by the variation of solvent and by pressure programming (in addition to temperature programming) during a separation (Schoemakers and Uunk, 1992).

In supercritical fluid chromatography, the mobile phase is a substance maintained at a temperature a few degrees above its critical point. The physical properties of this substance are intermediate to those of a liquid and of a gas at ambient conditions. Hence, it is preferable to designate this condition as the supercritical phase.

In a chromatographic column, the supercritical fluid usually has a density about 1/3–1/4 that of the corresponding liquid when used as the mobile phase; the

diffusivity is about 1/100 that of a gas and about 200 times that of the liquid. The viscosity is of the same order of magnitude as that of the gas. Thus, for chromatographic purposes, such a fluid has more desirable transport properties than a liquid. In addition, the high density of the fluid results in a 1000-fold better solvency than that of a gas. This is especially valuable for analyzing high-molecular-weight compounds.

A primary advantage of chromatography using supercritical mobile phases results from the mass transfer characteristics of the solute. The increased diffusion coefficients of supercritical fluids compared with liquids can lead to greater speed in separations or greater resolution in complex mixture analyses. Another advantage of supercritical fluids compared with gases is that they can dissolve thermally labile and nonvolatile solutes and, on expansion (decompression) of this solution, introduce the solute into the vapor phase for detection. Although supercritical fluids are sometimes considered to have superior solvating power, they usually do not provide any advantages in solvating power over liquids given a similar temperature constraint. In fact, many unique capabilities of supercritical fluids can be attributed to the poor solvent properties obtained at lower fluid densities. This dissolution phenomenon is increased by the variability of the solvent power of the fluid with density as the pressure or temperature changes.

The solvent properties that are most relevant for supercritical fluid chromatography are the critical temperature, polarity, and any specific solute-solvent intermolecular interactions (such as hydrogen bonding) that can enhance solubility and selectivity in a separation. Nonpolar or low-polarity solvents with moderate critical temperatures (e.g., nitrous oxide, carbon dioxide, ethane, propane, pentane, xenon, sulfur hexafluoride, and various Freons) have been well explored for use in supercritical fluid chromatography. Carbon dioxide has been the fluid of choice in many supercritical fluid chromatography applications because of its low critical temperature (31°C , 88°F), nontoxic nature, and lack of interference with most detection methods (Lundanes et al., 1986).

At the high pressure applied with supercritical fluid chromatography, *n*-butane and *n*-pentane are good solvents even for polar compounds. Carbon dioxide (CO_2) is only a poor to fair solvent for most high-molecular-weight petroleum fractions, but it has the additional virtue of being easily removed from the fractions. It permits the use of a flame ionization detector (FID) for supercritical fluid chromatography. The flame ionization detector provides a uniform response over a wide range of sample compounds and comes closest to being a true mass detector. Carbon dioxide is also the solvent of choice for the combination of supercritical fluid chromatography and mass spectrometry. Commercial equipment for analytical as well as preparative supercritical fluid chromatography separations is available.

Despite these advantages, supercritical fluid chromatography has only begun to have its potential realized when applied to petroleum, such as the determination of aromatic and polynuclear aromatic constituents in diesel fuel (ASTM D-5186).

However, the technique has not yet had its potential realized for application to heavy oil and bitumen or their respective high-molecular-weight fractions. One reason is the tendency of the restrictor to plug. The restrictor is needed to maintain the required high pressure throughout the entire column and consists either of a short, very fine capillary or a plate with a tiny hole positioned at the outlet. Even if complete plugging of the restrictors can be prevented, molecular clusters may still form in it and then cause spikes in the flame ionization detector output. These annoyances become worse with increasing sample molecular weight and polarity and, therefore, with increasing sample atmospheric equivalent boiling point (AEBP).

Although the method (ASTM D-2549) is generally limited to naphtha and light gas oil samples and to samples having a vapor pressure sufficiently low to permit sampling at ambient temperatures, the indications are that supercritical fluid chromatography will find wide applicability to the problems of identification of the higher-molecular-weight species in petroleum (Campbell and Lee, 1986; Chang et al., 1988; Schwartz et al., 1988; Smith et al., 1988).

The sample is injected into a supercritical fluid chromatograph (SFC), equipped with a column of limited efficiency, which separates the hydrocarbons into saturated (nonaromatic) and aromatic compounds. Because of its similar response to both saturated and aromatic compounds, a flame ionization detector is used to detect the components. At constant pressure and temperature, the area under the chromatogram is measured as a function of retention time.

10.9. THIN-LAYER CHROMATOGRAPHY

Column chromatography made separations possible that were otherwise impossible at the time, but complete separation usually required from 1 day to several weeks. However, biochemists and natural product chemists had realized for some time that a piece of filter paper could be used instead of the column. The glass tube and the tightly packed columns could be eliminated, and the separation times were reduced, usually from a day or two to a few hours. One of the difficulties was that only cellulose could be used as an inert phase. Other difficulties included the fact that the paper was made of fibers that were thicker in some parts than others, which caused irregular flow rates and poorer separations, and the fact that the paper could be destroyed by strong acids or bases, so the color-developing reagents had to be in mild solutions. These problems severely limited the types of compounds that could be separated because a paper was needed that was made from uniform-sized particles, regularly spaced, and capable of withstanding strong acids and bases.

The principle of what we now know as *thin-layer chromatography* (TLC) was first developed in 1938 in a method developed as an alternate to paper chromatography. The method involved dusting alumina (Al_2O_3) on to a glass plate. The

particles were uniform and inert to acids, but the dust would blow or wash away unless extreme care was taken, so a photograph of the results had to be obtained. There was no way to store the plates. The method did not receive attention as an analytical technique until a method was described to produce uniform-thickness, thin layers of silica gel (SiO_2) held onto glass plates with 7–8% of plaster of Paris (CaSO_4) (Stahl et al., 1956). This concept formed the basis of current procedures and reduced separation times to 10–30 min.

The apparatus commonly used is a small glass jar with a screw-cap lid and may or may not have filter paper placed around the walls on the inside. The sample, one to two drops, is placed on a single spot about 2 cm from one end of the plate, and the spot is indicated with a pencil mark. A scratch mark is made on the coating 12 cm from the bottom end. The developing solvent is added to the developing jar to a height of about 1 cm. The plate is inserted, sample end down, and the jar is closed to help maintain a solvent-saturated environment. When the solvent has risen to the 12 cm mark by capillary action (10–30 min), the plate is removed. The solvent is allowed to evaporate or is dried with a hair dryer. The plate then is sprayed with a reagent that will form a color with the desired compounds. After spraying, colored spots become visible, and the distance they have moved compared to the solvent front is measured. The mechanism for the separation is most likely a combination of adsorption and partition. If essentially round spots form that are separated from each other, then the separation is primarily partitioning. If tailing occurs, then adsorption is a major factor.

This technique is perhaps one of the most ignored techniques available to the petroleum analytical chemist. It offers identification of a wide variety of compounds and compound type. Although still widely used by biochemists and by natural product chemists, its revival by in the field of petroleum analysis is perhaps overdue.

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CHAPTER

11

STRUCTURAL GROUP ANALYSIS

11.1. INTRODUCTION

Structural group analysis is the determination of the statistical distribution of the structural elements in petroleum, heavy oil (and heavy feedstocks such as bitumen and residua), and their respective fractions, irrespective of the way in which the *elements* are combined in molecules. Thus structural group analysis occupies a position midway between ultimate analysis (Chapter 4), in which atoms are the components, and molecular analysis (Chapter 2), in which molecules are the components. A method for structural group analysis seems to be complete only if structural elements are chosen in such a way that the sum of all elements equals 100% (or unity), for instance, by considering the distribution of carbon in aromatic, naphthenic, and paraffinic locations in petroleum, its fractions, and products.

Structural group analysis has been widely applied to the analysis of petroleum, heavy oil, bitumen, residua and their respective fractions. Comparative data have been collected pertaining to the character of these feedstocks that are often helpful in identifying products of unknown origin or in giving valuable indications concerning their manufacture. It is also claimed that, when more thorough knowledge of hydrocarbon types is required, structural group analysis may offer a means of following physical separation methods, such as distillation, solvent treatment, or chromatography, as well as the effects of thermal processes. However, structural group analysis may only provide average structural parameters, leaving much of the conclusions open to inspired guesswork.

As already noted (Chapter 2) but stated again here to emphasize the complexity of petroleum, heavy oil, and bitumen, the precursors to petroleum are as diverse as the plant chemicals themselves, and it must be recognized that there may have been some evolution of these chemicals over geological time as plants, and their constituents, evolved to modern-day counterparts. This is not to suggest that petroleum is a collection of plant chemicals and should be considered as a composite of carbohydrates, proteins, fatty acids, and any other chemical that can be derived from the pages of a natural product textbook!

Indeed, the constituents of the original precursor soup (*protopetroleum*) have undergone considerable change through chemical and physical interactions with their environment. Furthermore, local and regional variations in the nature of

the original plant precursors and in the maturation conditions offer a means of variation of petroleum from field to field. Thus a derivative of a chemical entity that is *predominant* in petroleum from one field may be an entity of somewhat lesser importance in another crude oil, even in crude oils of one particular type.

Although gas-liquid chromatography and other techniques (Chapter 10) have been applied successfully to the identification of a considerable number of petroleum constituents, they are mainly limited to the so-called front end, that is, the volatile portion, of petroleum. Because the majority of crude oils and heavy oils contain significant proportions of a nonvolatile residuum (bitumen being predominantly nonvolatile), it is not possible to identify individual components in this part of the feedstock by a technique that requires some degree of volatility of the constituents. It is because of this that other methods of identification have been pursued. This is where structural group analysis has played a valuable role if not sometimes a questionable role. To qualify the term *questionable role*, it is not the methods of structural group analysis that are at error because of the various inherent assumptions in each method but it is the means by which the data are treated by the investigators. Using the data too literally and forgetting that the term *average structure* cannot be always representative of the *true structure* as well as behavioral characteristics is the major issue. But to continue.

Methods for structural group analysis usually involve the determination of physical constants of the sample. However, because there is no simple relation between physical properties and chemical composition, a reliable correlation can only be obtained by studying properties of a great variety of oil fractions or pure compounds according to exact methods, laborious though that may be. The data collected statistically in this way may form the basis for chemical analysis by physical constants. The better the representation and the greater the number of these basic data, the more reliable the resulting method for structural group analysis will be. However, it should be remembered that structural group analysis is not the ultimate answer when applied to the heavier petroleum fractions or residua. Nevertheless, its importance lies in the straight correlation existing between the information derived from such analysis and physical properties; it is often sufficient to get an overall description of the material in terms of its average structural group composition.

The predominant feedstocks for structural group analysis are the high-boiling fractions of petroleum, heavy oil, resins and asphaltenes, petroleum products (asphalt), and residua. The result is the identification of the constituents of petroleum by molecular type may proceed in a variety of ways but generally can be classified into three methods: (1) spectroscopic techniques, (2) chemical techniques, and (3) physical property methods. Various structural parameters are derived from a particular property by a sequence of mathematical manipulations. It is difficult to completely separate these three methods of structural elucidation, and there must, by virtue of need and relationship, be some overlap.

This leads to analysis of the samples in terms of groups of hydrocarbons, and four classes are generally recognized:

Aromatic if it contains at least one aromatic ring.

Olefinic if it contains at least one olefinic bond.

Naphthenic if it contains at least one naphthenic ring.

Paraffinic if it contains neither an aromatic, a naphthenic ring, nor an olefinic double bond.

Aromatic hydrocarbons are also subdivided according to *aromatic type*, a term that describes compounds having the same number and grouping of aromatic rings. If an aromatic hydrocarbon contains two aromatic rings, three types may be distinguished:

1. The rings may be condensed, that is, fused together, to form the naphthalene nucleus.
2. The rings may be joined by an inter-ring bond as in the biphenyl nucleus.
3. The rings may be separated by one or more nonaromatic carbon atoms, such as diphenylmethane ($C_6H_5CH_2C_6H_5$) or dibenzyl ($C_6H_5CH_2CH_2C_6H_5$).

This nomenclature is open to extension to polynuclear aromatic compounds with more than two aromatic rings. Alkyl chains and naphthene rings are generally not considered in discussions of aromatic type. The method must also recognize combined hydrocarbon systems such as *naphtheno-aromatic compounds*, that allow for the fact that in many cases:

$$\begin{aligned} \%w/w \text{ aromatics} + \%w/w \text{ olefins} + \%w/w \text{ naphthenes} \\ + \%w/w \text{ paraffins} = >100\% \end{aligned}$$

There are two ways of reporting the results of a structural group analysis. One method is to determine the number of rings or other structural groups in terms of the average number of aromatic rings (R_A) and naphthene rings (R_N), and the total number of rings ($R_T = R_A + R_N$) is designated ring content. The other method is to determine the number of carbon atoms in aromatic (% C_A), naphthenic (% C_N), and paraffinic (% C_P) structures, all expressed per 100 carbon atoms in the sample. These data are designated as the *carbon distribution*, and if the molecular weight of the sample is known and if an assumption is made about the type of rings present, the ring content can be recalculated as carbon distribution; the converse is also applicable. Thus two terms, *carbon distribution* and *molecular weight* (both of which are averages), can then lead to derivation of a *hypothetical average molecule*.

It is always the case that when mathematical manipulations are used to derive *average structures*, the structures will only be as reliable as the assumptions used for the mathematical procedure. Then the literal interpretation that leads to the conclusion, and the insistence, that such structures exist in the sample only leads to more confusion. Representation is one matter. Adherent belief is another! Indeed, the complexity of the nonvolatile constituents of petroleum makes the construction of average structures extremely futile and, perhaps, misleading.

As noted, caution is advised here because such a molecule containing the structural groups in the proportions found by structural group analysis will not exist and may be difficult to use in determining the behavioral characteristics of the sample. The end results of these methods are *indications* of the *structural types* present in the material.

This chapter presents methods that can be applied to study the makeup of the feedstock in terms of chemical structures as well as methods that might be preferred for refining. The chapter deals with the older physical property methods that were used in the early days of structural group analysis, some of which are used even now. The evolution of the available spectroscopic techniques that could be applied to structural group analysis commenced in the 1960s, and these are included in the section following the physical property methods. Not all (in fact, very few) of these methods are recognized as standard methods, but they have received and continue to receive wide application in the analytical and research laboratories of the petroleum industry. It is this fact that makes their inclusion here essential.

11.2. PHYSICAL PROPERTY METHODS

There have been many proposals for the structural group analysis of petroleum and petroleum products, which are usually based on inspection of the elemental analyses and physical properties of the material. The overall result has been the acceptance of several of these methods on the basis of their convenience and/or relative simplicity, and these methods are described here.

11.2.1. Direct Method

The *direct method* (Vlugter et al., 1935a), so called because it involves direct determination of the required physical properties of the sample, is unlike other methods insofar as it does not usually require prior separation of the sample into aromatic and saturated fractions.

Thus, by means of elemental analysis (Chapter 4) and molecular weight determination (Chapter 12) before and after hydrogenation of the sample, the percentage of carbon in aromatic structures (%C_A) and the average number of rings (R_T) can be estimated. If an oil is hydrogenated so that only aromatic rings are converted

into naphthalene rings, each aromatic carbon atom takes up one hydrogen atom. Therefore,

$$\%C_A = 1191(H'M' - HM)/(100 - H)M$$

where H is the percentage hydrogen of the oil fraction, M is the average molecular weight, and H' and M' are the corresponding data for the hydrogenated product.

In several' cases the molecular weights can be omitted because the difference between M and M' may be negligible. The hydrogen content of the hydrogenated product, which is presumed to contain naphthenic and paraffinic carbon only, is an exact measure of the number of rings. As compared with paraffins, each ring closure involves a reduction by two hydrogen atoms. If R_T is the number of rings of the *hypothetical molecule*,

$$R_T = 1 + (0.08326 - 0.005793H')M'$$

To derive a complete set of carbon distribution and ring content figures from $\%C_A$ and R_T , an assumption must be made about the type of rings present. It is generally assumed that all rings are six membered and, in the case of the polycyclic materials, are kata-condensed; this type of condensation only occurs in such a way that the rings have two carbon atoms in common, as, for example, naphthalene, anthracene, or tetracene. However, the natural product origins of petroleum do not support the occurrence of systems based on anthracene, and tetracene is now considered less likely than the occurrence of systems based on phenanthrene and chrysene in crude oil. The natural product precursors of petroleum (Speight, 1999) are considered more likely to produce the angular- or peri-condensed aromatic systems.

For C_R , that is, the average number of ring carbon atoms per molecule, assuming that only kata-condensed six-membered rings are present,

$$C_R = 4R_T + 2R_{TS}$$

where R_{TS} is the number of *substantial* rings ($R_{TS} = R_T$ if < 1 and $R_{TS} = 1$ if $R_T > 1$). In a *kata-condensed system*, it is possible to differentiate between the rings insofar as one ring (a substantial ring) has six carbon atoms and the additional rings contribute only four carbon atoms each.

Thus the percentage carbon in ring structures is given by the expression

$$\%C_P = 240,200(2R_T + R_{TS})/M(100 - H)$$

and the carbon distribution is

$$\%C_P = 100 - \%C_R$$

$$\%C_N = \%C_R - \%C_A$$

where C_N is naphthalene carbon and C_A is aromatic carbon. Furthermore, because

$$\%C_A = 240,200(2R_A + R_{AS})/M(100 - H)$$

where R_{AS} is the number of substantial aromatic rings ($R_{AS} = R_A$ if $R_A < 1$ and $R_{AS} = 1$ if $R_A > 1$), then for $R_A < 1$,

$$R_A = \%C_A M(100 - H)/720,600$$

and for $R_A > 1$,

$$R_A = [\%C_A M(100 - H)/480,400] - 0.5$$

The naphthalene ring content is deduced from the relationship

$$R_N = R_T - R_A$$

It is perhaps unfortunate that the direct method does not require prior separation into fractions based on hydrocarbon type. It is also unfortunate that the method is also based on the assumption that heteroelements (e.g., nitrogen, oxygen, and sulfur) are not present in the petroleum sample. However, if these elements are present, corrections can be applied, but this detracts from the basis of the method because rings containing heteroelements may be cleaved during the hydrogenation process (Speight, 2000). Corrections may also need to be applied to dissociate the method from the assumption that the polynuclear systems are kata-condensed systems (e.g., anthracene) rather than peri-condensed systems (e.g., phenanthrene). Nevertheless, the method does provide a means whereby $\%C_A$ and R_T can be determined and has been considered one of the more reliable methods for structural group analysis.

11.2.2. Waterman Ring Analysis

This method (Vlugter et al., 1935b, 1939) requires the determination of the density (Chapter 4), refractive index (Chapter 6), aniline point (Chapter 5), and molecular weight (Chapter 12). In essence, the elemental analysis used in the direct method is replaced by the specific refraction.

Thus, because molecular refraction r_M is additive for a hydrocarbon C_xH_y ,

$$r_M = Mr^{20}_D = xr_C = yr_H$$

where r_C and r_H represent the atomic refraction of carbon and hydrogen, and M is the molecular weight. Because:

$$y = MH/100.8$$

and

$$x = M(100 - H)/1201.0$$

where H is the percentage of hydrogen, then

$$\%H = (100.8 \times 1201.0r^{20}_D - 100.8r_C)/(1201r_h - 100.8r_c)$$

Correlation of hydrogen content and specific refraction for a series of petroleum fractions leads to the relationship:

$$\%H = 110.48r^{20}_D - 22.078$$

Because the total number of rings R_T is given by

$$R^T = 1 + (0.08326 - 0.005793H')M'$$

then

$$R_T = 1 + (0.2122 - 0.6401r^{20}_D)M$$

and because

$$\%C_R = 240.200(2R_T + R_{TS})/M(100 - H)$$

then

$$\%C_R = 240,200(2R_T + 2R_{TS})/M(77.922 - 100.48 \cdot r^{20}_D)$$

$$R_{TS} = R_T, \quad \text{if } R_T < 1$$

and

$$R_{TS} = 1 \quad \text{if } R_T > 1$$

Thus a relation among specific refraction, molecular weight, and percentage carbon in naphthalene rings for saturated hydrocarbons or atomic- and olefin-free oil fractions can be defined (Fig. 11.1). Similarly, a graphic relation among aniline point, specific refraction, and molecular weight of saturated oil fractions has also been defined (Fig. 11.2).

The sources of error in the Waterman ring analysis are derived from the specific refraction, the limited molecular weight range (200–500), and the errors that are

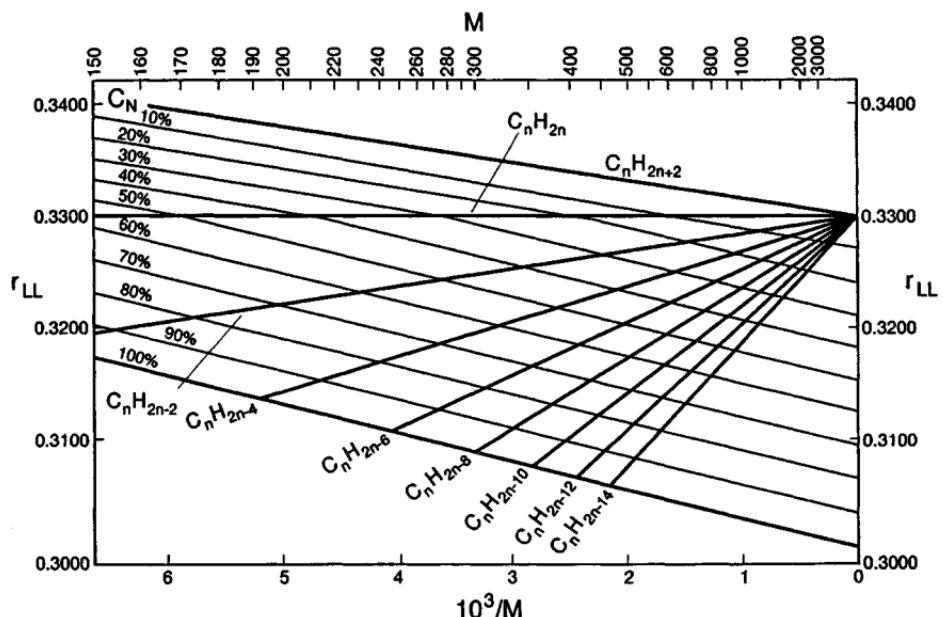


Figure 11.1. Graphical relationship used for the Waterman ring analysis.

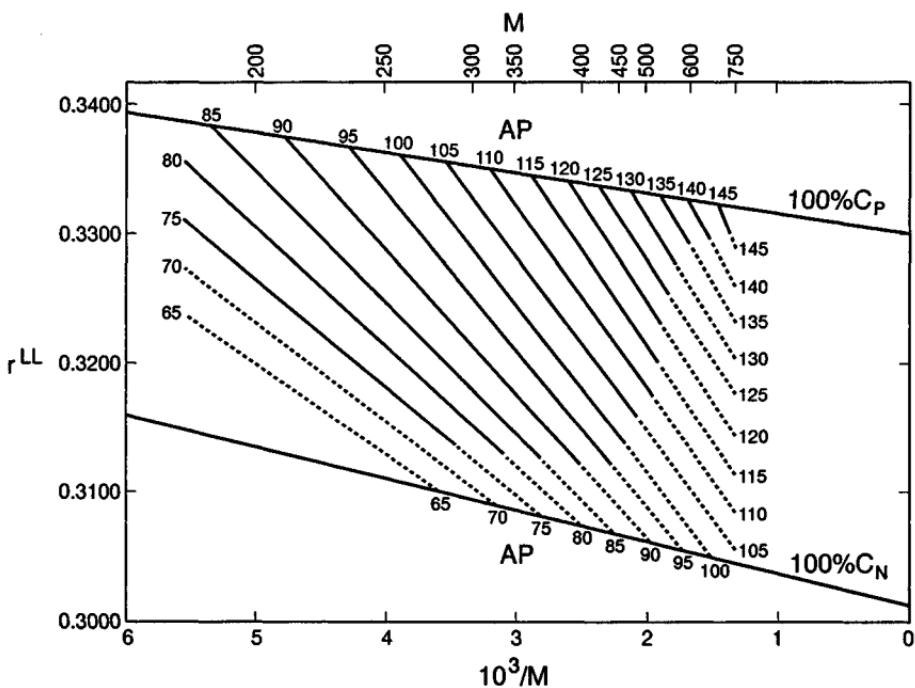


Figure 11.2. Alternate graphical relationship used for the Waterman ring analysis.

inherent in the aniline point determination because of the complexity and color of the sample. Nevertheless, even though the accuracy of the method is questionable, it has found wide acceptance and use.

11.2.3. Density Method

This method is based on the use of the density d (Chapter 4), specific refraction r_{LL} (Chapter 6), and the molecular weight M (Chapter 12). This method is based on correlation of oil composition, determined by the direct method (Section 11.2.1), and the procedure used for this method is analogous to that employed for the Waterman ring analysis, but the main difference is that the density is used instead of the aniline point.

Thus the density corresponding to the observed molecular weight M and specific refraction r_{LL} is determined (Fig. 11.3); the difference Δd between this value and the observed value is noted. Thus

$$\%C_A = 420\Delta d/(1 + 3.2\Delta d)$$

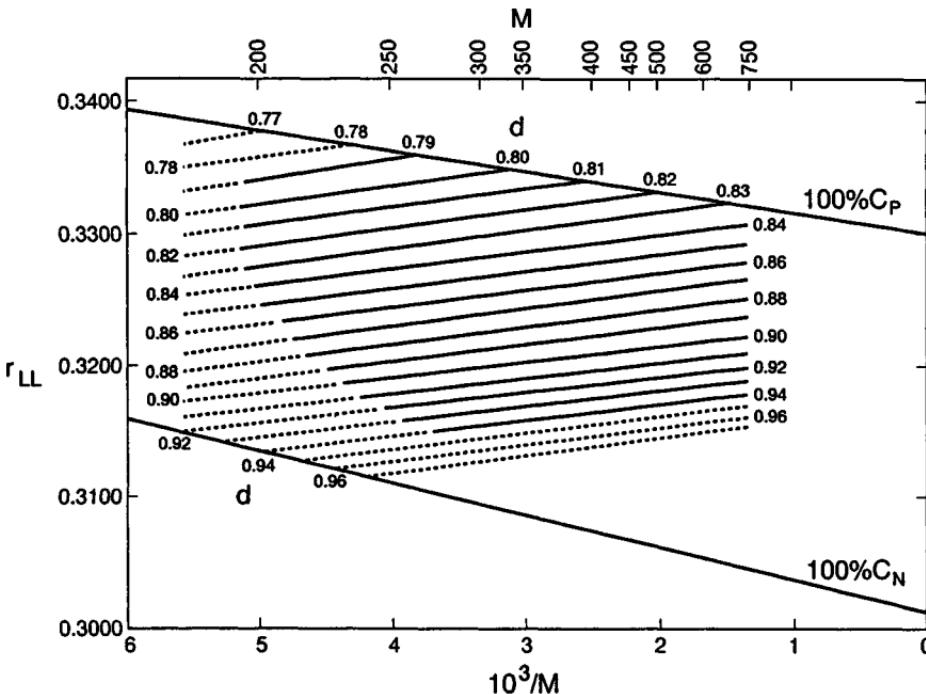


Figure 11.3. Graphical relationship used for structural analysis by the density method.

and C_R is obtained graphically; thence,

$$\%C_P = 100 - \%C_R$$

$$\%C_N = \%C_R - \%C_A$$

The experimental procedure of this method is simplified compared to that of the Waterman ring analysis and the applicability is more general. In addition, there seems to be better agreement with data obtained by the direct method. Disadvantages, which are also inherent in the Waterman ring analysis, are that the molecular weight range is limited to 200–500 and extrapolation of the data to the higher range is uncertain; indeed, a high aromatic content causes the specific refraction to fall outside the correlation. The accuracy of the density method is in general fairly good, although according to the basic data used the application should be limited to fractions with $\%C_A < 1.5\% C_N$ or with $R_A < 0.5 R_T$.

11.2.4. *n-d-M* Method

The *n-d-M* correlation (ASTM D-3238) uses, as the name implies, the refractive index *n* (Chapter 6), density *d* (Chapter 4), and molecular weight *M* (Chapter 12) to estimate the percentage of the total carbon distribution in aromatic rings ($\%C_A$), naphthenic rings ($\%C_N$) and paraffin chains ($\%C_P$) (Table 11.1). The sulfur content of the sample should also be determined because there are differences in the calculation for samples having sulfur contents below or above 0.206% by weight. The *n-d-M* method is especially intended for petroleum fractions boiling above the gasoline range (b.p. $>200^\circ\text{C}$, $>392^\circ\text{F}$) and for similar samples that result from extraction, hydrogenation, or thermal treatment.

The validity of the method is good for petroleum fractions with up to $\%C_R = 75\%$ (aromatic + naphthenic), provided that $\%C_A$ (as found by the *n-d-M* method) is not higher than 1.5 times $\%C_N$. Also, the method is also valid for samples containing up to four rings per molecule if not more than half of these are aromatic. Application to samples with a relatively high naphthene ring content may cause minor, but not serious, errors. Although the presence of heteroelements (nitrogen, oxygen, and sulfur) influences the accuracy, the method is applicable to samples containing nitrogen (up to 0.5% by weight), oxygen (oxygen up to 0.5% by weight), and sulfur (up to 2% by weight).

11.2.5. Dispersion-Refraction Method

This method (Deanesly and Carleton, 1942) is analogous to the direct method, but the hydrogenation and the examination of the hydrogenated product are replaced by the determination of the following: carbon and hydrogen content (Chapter 4),

Table 11.1. Formulae for the Calculations Used in the n-d-M Method

Measurements at 20°C		Measurements at 70°C	
Calculate:		Calculate:	
$v = 2.51(n - 1.4750) - (d - 0.8510)$		$x = 2.42(n - 1.4600) - (d - 0.8280)$	
$w = (d - 0.8510) - 1.11(n - 1.4750)$		$y = (d - 0.8280) - 1.11(n - 1.4600)$	
%C _A	if v is positive: $\%C_A = 430v + 3660/M$ if v is negative: $\%C_A = 670v + 3660/M$	%C _A	if x is positive: $\%C_A = 410x + 3660/M$ if x is negative: $\%C_A = 720x + 3660/M$
%C _R	if w is positive: $\%C_R = 820w - 3S + 10,000/M$ if w is negative: $\%C_R = 1440w - 3S + 10,600/M$	%C _R	if y is positive: $\%C_R = 775y - 3S + 1150/M$ if y is negative: $\%C_R = 1400y - 3S + 12100/M$
R _A	if v is positive: $R_A = 0.44 + 0.055Mv$ if v is negative: $R_A = 0.44 + 0.080Mv$	R _A	if x is positive: $R_A = 0.41 + 0.055Mx$ if x is negative: $R_A = 0.41 + 0.080Mx$
R _T	if w is positive: $R_T = 1.33 + 0.146M(w - 0.005S)$ if w is negative: $R_T = 1.33 + 0.180M(w - 0.005S)$	R _T	if y is positive: $R_T = 1.55 + 0.146M(y - 0.005S)$ if y is negative: $R_T = 1.55 + 0.180M(y - 0.005S)$

S is the sulfur content in wt%.

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refractive index (Chapter 6), density (Chapter 4), molecular weight (Chapter 12), bromine number (Chapter 8), specific dispersion (Chapter 6), and specific refraction (Chapter 6) of the original fraction (Fig. 11.4).

The structural parameters obtained by this method are similar to those derived from the direct method, except that olefin double bonds (through use of the bromine number) are also measured (Table 11.2). In addition, the method can be used on materials derived from cracking processes because determination of the olefin content is provided for by inclusion of the bromine number.

However, the method is based on data derived from pure hydrocarbons having fewer than 18 carbon atoms per molecule, and the accuracy or interpretation of the data must be suspect when applied to systems containing more than 18 carbon atoms as well as heteroelements (nitrogen, oxygen, and sulfur).

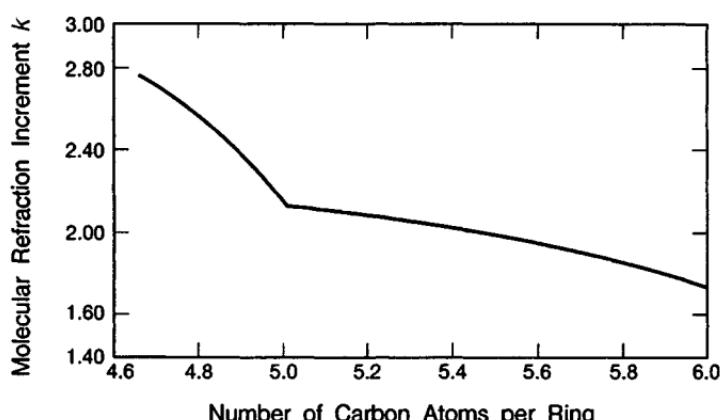
11.2.6. Density-Temperature Coefficient Method

This method utilizes the linear relationship between the temperature coefficient of density and the density (Chapter 4) for various series of hydrocarbons (Lipkin et al., 1946). Two calculations are performed and are based on density limitations.

Table 11.2. Calculations Used in the Dispersion-Refraction Method

Calculation		
1. Specific refraction	$r = (n^2 - 1)/d(n^2 + 2)$	0.3231
2. Specific dispersion	$s = (n_F - n_C)10^4/d$	131.6
3. Corrected hydrogen content	$y = 100H/(C + H)$	11.66
4.	$hk = 201.6(r - 0.2084 - 0.008421y)$	3.32
5. Unsaturation	$h = \left[\frac{hk}{0.811(S - 98)^{0.202}} \right]^{1.412}$	1.72
6. Molecular refraction increment	$k = hk/h = 3.32/1.72$	1.93
7. Olefinic unsaturation	$h_O = \text{bromine number}/79.3$	0.0
8. Aromatic unsaturation	$h_A = h - h_O$	1.72
9. Percentage aromatic carbon	$\%C_A = 1191h_A/(100 - y)$	23.2
10. Total ring content	$R_T = 1 + \frac{M(2.016 - 0.1403y)}{24.212} - \frac{Mh}{201.6}$	2.80
11. Number of carbon atoms per ring n_R (Fig. 6.6)		5.64
12. Percentage ring carbon	$\%C_R = 120,100R_T \times n_R/M(100 - y)$	85.9
13. Aromatic ring content	$R_A = C_A/n_R = h_A MM/n_R 100.8$	0.76
Results		
$\%C_A = 23.2$	$R_T = 2.80$	
$\%C_N = \%C_R - \%C_A = 62.7$	$R_A = 0.76$	
$\%C_P = 100 - \%C_S = 14.1$	$R_N = R_T - R_A = 2.04$	

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**Figure 11.4.** Graphical relationship used for structural analysis by the dispersion-refraction method.

In the first case, for the analysis of paraffin-naphthalene mixtures with a density below 0.861, it is assumed that in the density-density temperature coefficient diagram the portion of the intercept (at constant density) between the paraffin and naphthalene line is divided by the sample point into parts proportional to paraffin and naphthalene content. In this way the following equation for mixtures of paraffins and naphthalenes in the regions below 0.861 density was derived:

$$\text{Wt.\% rings} = [190.0d - 217.9 - 105dd/dt]/(0.593d - 0.249)$$

where d is the density at 20°C (68°F) and dd/dt is the change in density per degree change in temperature.

In the second case, for mixtures having a density above 0.861, it is assumed that there is an equal distribution of condensed and noncondensed naphthalenes. The sample point was assumed to divide the line between the limiting paraffin point and a point on the naphthalene ring line above 0.861 into parts proportional to paraffin and naphthalene content, and for this region the following formula was derived:

$$\text{Wt. rings} = [102.8d - 142.8 - 10^5dd/dt]/0.262$$

Simplification of the experimental procedure could be achieved by deriving the density coefficient from the molecular weight, which in turn can be estimated from other physical properties, such as the density (Chapter 4) and mid-boiling point (Chapter 5), or viscosity at 38°C (100°F) and 99°C (210°F) (Chapter 4). However, because:

$$-10^5dd/dt = 53.5 + 3360/M$$

if $d < 0.861$,

$$\text{Wt.\% rings} = [190.0d - 164.4 + 3360/M](0.593d - 0.249)$$

and if $d > 0.861$,

$$\text{Wt.\% rings} = (102.8d - 89.3 + 3360M)/0.262$$

For the analysis of samples containing aromatic compounds and no naphthalene rings, a procedure is followed that is quite analogous to the ring-chain analysis for naphthalenes. The line between the limiting paraffin point and a point of the aromatic ring line in the density-density temperature coefficient diagram is divided by the *sample point* (Fig. 11.5). It is assumed that the parts are proportional to aromatic ring and paraffinic chain content. The relationship among wt. aromatic ring, density coefficient, and density is only given graphically; graphs are used for condensed ring aromatics (Fig. 11.6), for noncondensed ring aromatics (Fig. 11.7), and for mixtures having an equal distribution of these two types (Fig. 11.8).

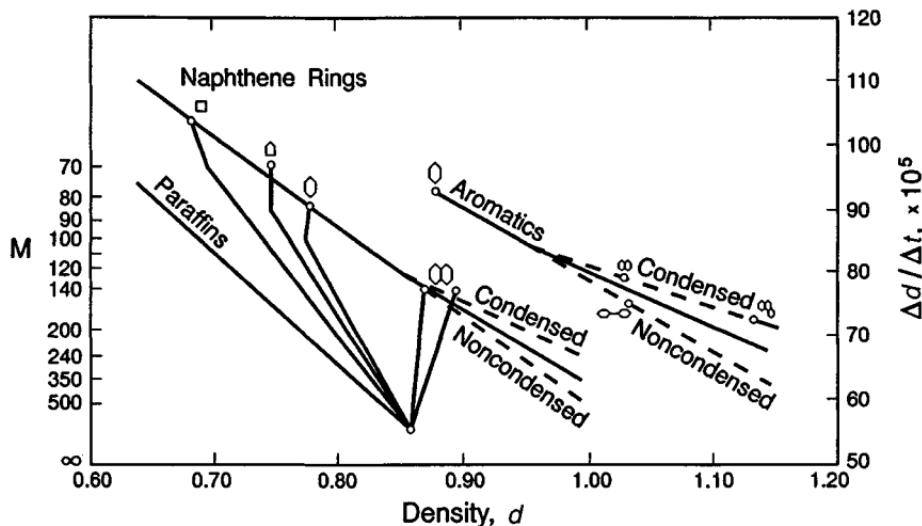


Figure 11.5. Density-temperature coefficients for various hydrocarbon series.

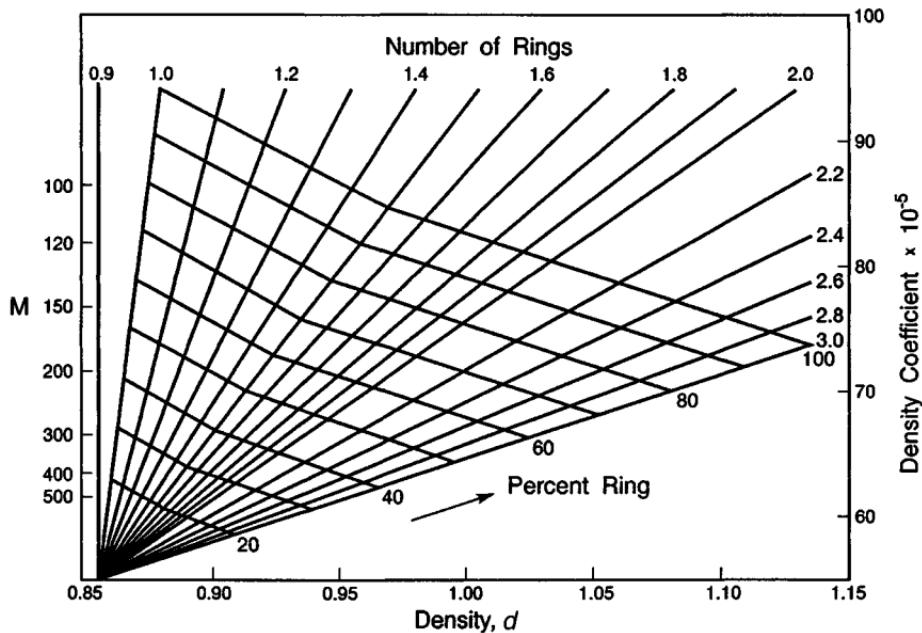


Figure 11.6. Graphical relationship used for structural analysis of polynuclear aromatic systems in the density-temperature coefficient method of structural group analysis.

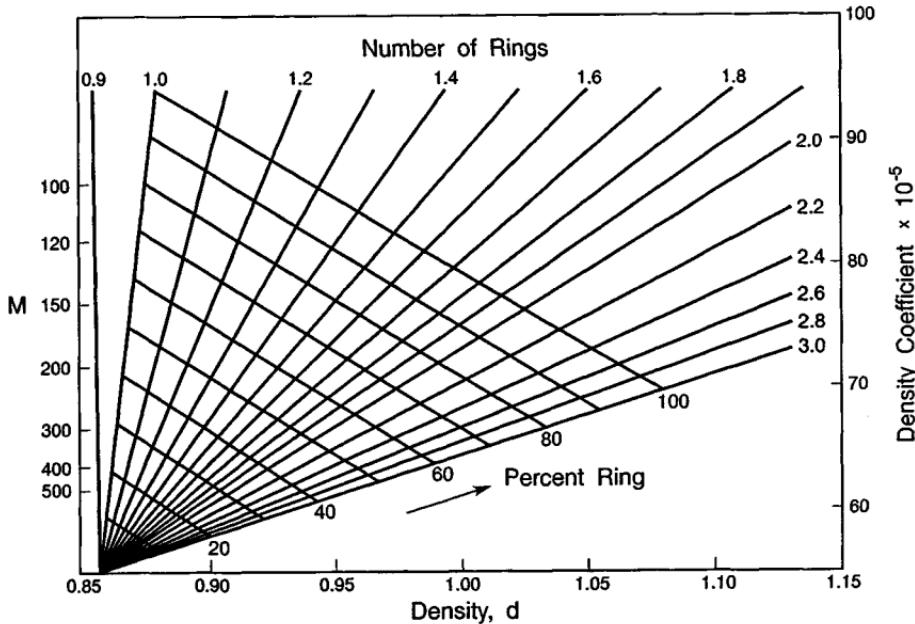


Figure 11.7. Graphical relationship used for structural analysis of noncondensed ring aromatic systems in the density-temperature coefficient method of structural group analysis.

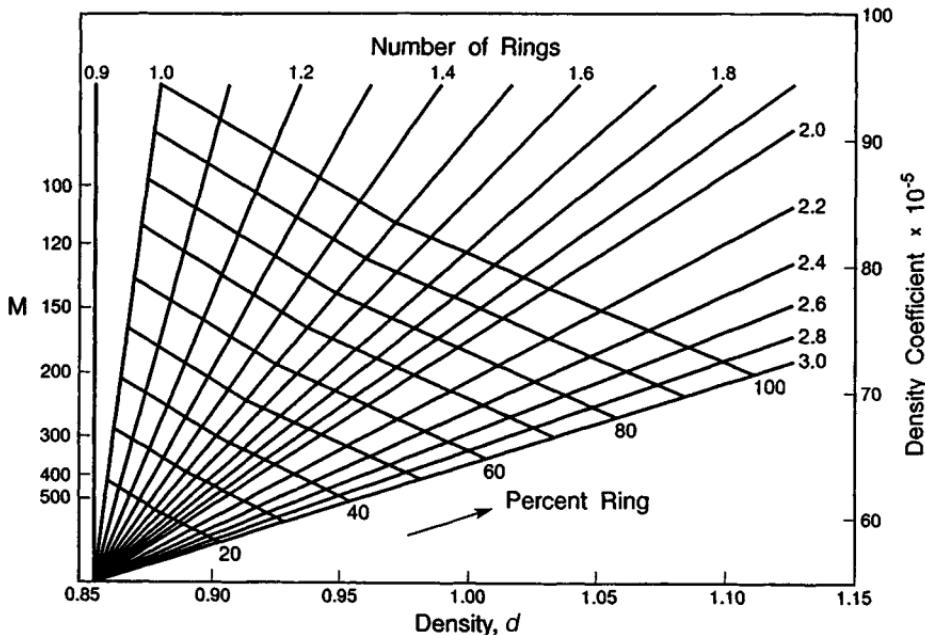


Figure 11.8. Graphical relationship used for structural analysis of mixtures of polynuclear aromatic systems and noncondensed ring aromatic systems in the density-temperature coefficient method of structural group analysis.

The applicability of the method for analyzing aromatic fractions is limited to fractions having no naphthalene rings along with the aromatic rings, although the method may be applied to alkylated aromatics.

11.2.7. The Molecular Weight-Refractive Index Method

The samples to be analyzed by the molecular weight-refractive index method must be separated beforehand into aromatic and paraffin-naphthalene fractions by, for example, silica gel adsorption chromatography (Chapter 10). As the name indicates, only the molecular weight M (Chapter 12) and the refractive index n^{20}_D (Chapter 6) are the required parameters, and by using data derived from use of pure hydrocarbons, the following relationships appear to hold:

Aromatic oils, noncondensed rings:

$$\begin{aligned}\%C_A &= \left\{ 1060[(n^{20}_D - 1.4750)M + 8.79]^{0.85} \right\} / M - 2 \\ &\quad + 1.01[(n^{20}_D - 1.4750)M + 8.79]^{0.85} \\ R_A &= 0.126[(n^{20}_D - 1.4750)M + 8.79]^{0.85}\end{aligned}$$

Aromatic oils, kata-condensed rings:

$$\begin{aligned}\%C_A &= \left\{ 2150[(n^{20}_D - 1.4750)M + 8.79]^{0.56} \right\} / M - 3 \\ &\quad + 2.3[(n^{20}_D - 1.4750)M + 8.79]^{0.56} \\ R_A &= 0.165[(n^{20}_D - 1.4750)M + 8.79]^{0.74}\end{aligned}$$

Mixtures of condensed and noncondensed rings:

$$\begin{aligned}\%C_A &= \left\{ [1650(n^{20}_D - 1.4750) + 8.79]^{0.67} \right\} / M - 2 \\ &\quad + 1.65[(n^{20}_D - 1.4750)M + 8.79]^{0.67} \\ R_A &= 0.151[(n^{20}_D - 1.4750)M + 8.79]^{0.78}\end{aligned}$$

Nonaromatic oils, condensed and noncondensed rings:

$$\begin{aligned}\%C_R &= \left\{ 2920[(n^{20}_D - 1.4750)M + 8.79]^{0.73} \right\} / M - 2 \\ &\quad + 0.57[(n^{20}_D - 1.4750)M + 8.79]^{0.86} \\ R_T &= 0.284[(n^{20}_D - 1.4750)M + 8.79]^{0.86}\end{aligned}$$

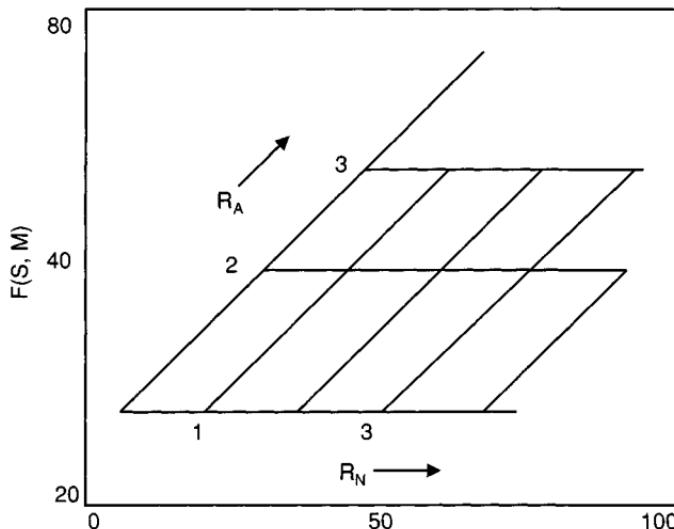


Figure 11.9. Graphical method used for structural group analysis.

Application of the $M \cdot n^{20}\text{D}$ method to saturated portions of oil fractions gives results that in general are in good agreement with those obtained by other methods.

11.2.8. Other Methods

There are several additional methods for structural group analysis that have been proposed but are not known by any specific name. Most are modifications of the named methods and were divided because of the need to apply such methods to, in some cases, higher-molecular-weight and/or real-life samples.

One method has also been proposed for determining the number of aromatic rings R_A and naphthenic rings R_N in aromatic fractions of petroleum and involves measurement of the molecular weight M (Chapter 4), density d (Chapter 4), and refractive dispersion s (Chapter 6). From the measured data, the functions:

$$F(s, M) = (s - 98)(M + 12)10^{-3}$$

and

$$F(d, M) = (d - 0.854)(M + 12)$$

are calculated, and R_A and R_N are estimated graphically (Fig. 11.9).

Indeed, the procedure is simple and rapid, and the method is claimed to be applicable to aromatic concentrates from both nondestructive distillation and cracking processes. Average deviations of 0.1 of an aromatic ring and about 0.2 of a naphthene ring are usual. If there are more than three aromatic rings per molecule, the

results are uncertain because of a lack of basic data and knowledge concerning the types of petroleum hydrocarbons with four or more aromatic rings. Saturated hydrocarbons, olefins, some noncondensed polycyclic aromatics, and nonhydrocarbons are reputed to introduce serious errors into the analysis.

Another methods include the derivation of a linear relation between percentage carbon in aromatic structure $\%C_A$, refractive index n^{20}_D (Chapter 6), density d_{20} , (Chapter 4), and aniline point (AP) (Chapter 5):

$$\%C_A = 1039.4n^{20}_D - 470.4d^{20} - 0.315AP - 1094.3$$

This formula holds good only if $\%C_A < 30$. When the calculated value for $\%C_A$ exceeds 30, a corrected value must be found by using the formula

$$\%C_{A(\text{corr})} = 0.5\%C_{A(\text{calc})} + 15$$

Alternatively, it has been suggested that the molecular weight determination (Chapter 12) of the n - d - M method be replaced by kinematic viscosity measurements (Chapter 4) leading to a n - d - V method.

An equation has been devised that is applicable to lubricating distillates that have not been subjected to thermal cracking, temperatures $< 350^\circ\text{C}$ ($< 660^\circ\text{F}$). If the naphthenic carbon is of the order of 25–75% of the total carbon, a relationship exists between the refractivity intercept (Chapter 6) (Kurtz and Ward, 1936, 1937; Kurtz and Headington, 1937) and the number of carbons in naphthenic locations (C_N):

$$\text{Refractivity intercept} = 1.0502 - 0.00020 \times \%C_N$$

Finally, it has also been proposed that for substances such as asphaltenes, which contain condensed ring systems, the following relationships be applied:

$$R = 0.11(9.9C - 3.1H - 3.70 + 1.5N + 14S - M/d)$$

where R is the number of rings, C , H , O , N , and S are the numbers of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms (Chapter 4), M is the molecular weight (Chapter 12), and d is the density (Chapter 4).

However, if it is not possible to determine the molecular weight, the relationship has been modified to

$$C/R = 9.2/(9.9 + 3.1H/C + 3.70/C + 1.5N/C + 14S/C - 1200/\%C, d)$$

where C/R is the ring condensation index, H/C , O/C , N/C , and S/C are the various atomic ratios calculated from elemental analyses, $\%C$ is the percentage of carbon obtained by elemental analysis, and d is the density.

Unfortunately, the method assumes that atoms other than carbon and hydrogen are not major components, olefins are absent, the number of rings is greater than one, and the rings are the fused naphthalene type rather than the biphenyl type.

11.3. SPECTROSCOPIC METHODS

The physical property methods of structural analysis described in the previous section have been augmented and complemented by use of a wide variety of instrumental techniques.

The application of spectroscopic methods to structural analysis is an innovation of the latter part of the twentieth century and has received considerable attention. As composition studies in petroleum advance to the higher-molecular-weight ranges, the physical nature of the material often requires that the structural analysis be performed by a more convenient and suitable technique. For example, gas-liquid chromatography (Chapter 10) may well suffice for the identification of the volatile constituents of petroleum, as well as for volatile petroleum products.

With the startling advances in spectroscopic techniques after World War II, chemists and technologists have been able to gain a better understanding of the chemical nature of petroleum and, therefore, of the chemical changes that occur during refining. Consequently, new fields of research have been opened involving the structural determinations of fossil fuels using spectroscopic techniques.

Each technique should be recognized for the particular capabilities that it offers and used in conjunction with one or more of the other methods described in this chapter. In addition, the structural data are usually obtained from a combination of two or more methods. This is preferred because a multidimensional approach yields more valuable information about a particular fraction than the data from one method alone.

It is the purpose of this section to review the spectroscopic methods that are used for the structural group analysis of petroleum, heavy oil, and bitumen, as well as their constituent fractions. This presentation of the spectroscopic and spectrometric methods is in keeping with the role that these techniques now play in the identification of the high-molecular-weight constituents of the various feedstocks. It is not intended to convey here that any one of these methods can be used for identification purposes. However, although these methods may fall short of acceptability as methods for the identification of individual constituents, they are recognized as methods by which an overall evaluation of the feedstock may be obtained in terms of molecular types. It is appropriate to describe these methods briefly at this point to place them in their context relative to the other methods already described.

11.3.1. Infrared Spectroscopy

Infrared absorption spectroscopy is an excellent method for providing detailed information about the chemical and functional group constitution of petroleum products (IP 429). Whether the material being examined is a single compound or a mixture, infrared absorption spectroscopy offers valuable information about the hydrocarbon skeleton and about the functional groups in petroleum with specific

Table 11.3. Bands Generally Observed in the Infrared Spectra of Petroleum, Heavy Oil, and Bitumen

Band		
cm ⁻¹	μ	Assignment
3030	3.30	Aromatic C—H stretching
2920	3.42	Methyl C—H stretching
2880	3.47	Methylene C—H stretching
1735	5.76	Carbonyl C=O
1700	5.88	Carbonyl C=O
1600	6.25	C=C and C=O (hydrogen-bonded)
1465	6.83	C—H bending
1380	7.25	C—H bending in methyl groups
1130	8.85	Sulfur-oxygen functions
1020	9.80	Sulfur-oxygen functions ^a
865	11.56	Aromatic C—H bending (out of plane)
815	12.27	
760	13.16	
735	13.61	

^aAlso aromatic ethers.

reference to the functional groups in the nonvolatile resin fraction and asphaltene fraction (Wen et al., 1978; Speight, 1994a, 1994b).

When properly prepared and scanned with suitable instruments, the infrared spectra of petroleum fractions show a number of well-defined bands (Table 11.3). For the purposes of structural group analysis, however, the bands at 1380, 1465, 2880, and 2920 cm⁻¹ are usually used. This allows an estimation of the number of methyl and methylene groups present in the samples.

Thus, initially, the absorptivity in grams per liter per centimeter is calculated as

$$a_b = A_b / cl$$

where a_b is the absorptivity ($\text{g/L} \times \text{cm}^{-1}$) at the wavelength b , A_b is the absorbance of the solution at wavelength b , c is the concentration of the solution (g/L), and l is the cell thickness in centimeters.

Following from this, the absorptivity per gram carbon in the standard group absorbing is derived in the following manner:

$$a_c = Ma_b / 12.01n$$

where a_c is the absorptivity (g/L cm^{-1}) per gram carbon of the type absorbing, M is the gram molecular weight, n is the number of carbon atoms of the type absorbing

per molecule, 12.01 is the gram atomic weight of carbon, and a_b is the absorptivity derived previously. By use of the a_c term for specific types of carbon (1.50 at 1465 cm^{-1} for methyl; 3.60–4.00 at 2880 cm^{-1} for methylene), the number of carbon atoms of that type present in the sample may be calculated.

Another infrared spectroscopic procedure that has been used to gain insight into the carbon distribution in petroleum residua and related materials involves determination of the molecular extinction coefficient, E , for the band under investigation.

$$E = (l/cl)\log(I_0/I)$$

where c is the molarity of the solution, l is the path length in centimeters, and I_0/I is determined directly from the infrared spectrum and is actually the ratio of the intensity of the incident light I_0 to the intensity of the transmitted light I .

The fraction of hydrogen atoms h_a attached to aromatic carbons can be derived in the following manner:

$$h_a = H_A/H_A + H_S$$

where H_A is the number of aromatic hydrogen atoms and H_S is the number of saturated hydrogen atoms.

$$h_a = [E_{3030}/(E_{3030} + E_{2920})]^k$$

where E_{3030} and E_{2920} are the extinction coefficients of the 3030 and 2920 cm^{-1} absorption bands, respectively. Studies with standard alkylaromatic compounds and polymers indicated that there was good agreement between the theoretical and observed hydrogen distribution when k was unity.

The proportion of carbon atoms in methyl groups to the total number of carbon atoms can be determined in a similar manner. Thus,

$$C_{\text{Me}}/C_T = H/C \times C_{1380}/E_{3030} + E_{2920}$$

where C_{Me} is methyl carbon, C_T is total carbon, H/C is the atomic hydrogen-carbon ratio determined from elemental analysis, E_{1380} is the extinction coefficient of the band at 1380 cm^{-1} , and E_{3030} and E_{2920} are the extinction coefficients of the bands at 3030 and 2920 cm^{-1} , respectively.

Historically, the first use of infrared spectroscopy in a quantitative approach to the structural analysis of petroleum occurred in 1956 (Brandes, 1956) in which the distributions of aromatic, naphthenic, and paraffinic carbon were calculated for a series of gas oils. Following from this, the 1610 cm^{-1} and 720 cm^{-1} infrared

absorption bands have also been used to calculate the carbon distribution (Fischer and Schramm, 1959).

The conclusion was that asphaltenes consist of condensed aromatic ring systems substituted by paraffinic chains, with naphthenic rings also present, but only to a minor extent. Similar results were also reported for other bituminous and asphaltic materials (Chelton and Traxler, 1959; Romberg et al., 1959). However, it was shown that use of the 1600 cm^{-1} band for estimation of weight percent aromatic carbon has, in some instances, led to values in excess of 100% and any discrepancy may arise from interference by carbonyl groups attached to the aromatic system.

Since that time, infrared spectroscopy has also been used extensively in the elucidation of the structural entities present in asphaltenes and resins (Erdman, 1965; Witherspoon and Winniford, 1967; Monin and Pelet, 1984; Tripathi et al., 1984; Hasan et al., 1988; Speight, 1994a; Speight, 1999).

For example, the bands at about 3030 cm^{-1} have been assigned to aromatic carbon-hydrogen stretching and have demonstrated that this band may shift to values as high as 3052 cm^{-1} with decreasing ring number. In addition to the carbonyl functions, the infrared spectra of asphaltenes show a strong carbon-hydrogen band at 2940 cm^{-1} , a peak characteristic of CH_2 groups at 1470 cm^{-1} , and peaks for methyl groups at 1380 cm^{-1} . The group of peaks at about 760 , 814 , and 870 cm^{-1} are believed to be caused by substituted aromatic ring structures. The *aromatic* ring band at 1600 cm^{-1} is preeminent, whereas the broad and strong absorption between 1330 and 1110 cm^{-1} has been assigned to oxygen-containing species (Stewart, 1957). Peaks at 1300 and 1135 cm^{-1} have been attributed to sulfur-oxygen bonds but a characteristic peak at 1040 cm^{-1} has not been adequately diagnosed. The band at 725 cm^{-1} , usually attributed to methylene chains having four or more units, is often present, but varies in intensity depending on the petroleum source. The band at 740 cm^{-1} has been suggested to arise from alkyl-benzenes and the band at approximately 1600 cm^{-1} has been assigned to aromatic carbon-carbon bonds (Nagy and Gagnon, 1961; Millson, 1967).

In addition, the aromaticity (1600-cm^{-1} band) of the asphaltenes is significantly greater than that of the maltene fraction but, from infrared spectroscopy, increases only slightly with molecular size (Altgelt, 1965). This is in general agreement with the data from elemental analysis and from carbon-13 magnetic resonance spectroscopy, where the aromaticity approaches an asymptotic limit for asphaltenes precipitated by *n*-decane (Speight, 1994b) although the distribution of aromaticity appears to be dependent on the functional types within an asphaltene (Gould and Long, 1986).

Thus the application of applied infrared spectroscopic techniques to the elucidation of the structures of petroleum resins and asphaltenes illustrated the presence of many structural groups and their relative positions to one another (Yen and Erdman, 1962). These studies also were suggestive of a type of ring condensation for petroleum asphaltenes different from that found in coal and it was concluded that

petroleum asphaltenes were primarily peri-condensed, like phenanthrene, whereas the coals were kata-condensed, like anthracene.

The concept of a different type of aromatic system being present in petroleum compared with coal is not too unrealistic in view of the potential difference in the precursors as well as the differences in maturation paths. However, there has been the suggestion that kata-condensed aromatics are present in petroleum and peri-condensed aromatics are present in coal (Williams and Chamberlain, 1963; Friedel et al., 1968).

Further development of the method for structural group analysis, using a large number of hydrocarbons, allowed three chemical and two physical properties to be expressed in terms of five structural groups (Montgomery and Boyd, 1959; Boyd and Montgomery, 1963). The chemical properties included the carbon and hydrogen content as well as the number of aromatic carbons present per molecule, and the physical properties required for the analysis are the molar volume and molar refraction. However, it was concluded that the 1600 cm^{-1} absorption band was not capable of producing reliable estimates of aromatic carbon in the heavier feedstocks because the fractions are of such complex composition. The results did indicate that the infrared data were self-consistent for the estimation of methylene and methyl groups in the bituminous fractions.

Conventional *infrared spectroscopy* also yields information about the functional features of various petroleum constituents. For example, infrared spectroscopy aids in the identification of N–H and O–H functions, the nature of polymethylene chains, the C–H out-of-place bending frequencies, and the nature of any polynuclear aromatic systems (Yen, 1973). With the recent progress of *Fourier transform infrared (FTIR) spectroscopy*, quantitative estimates of the compound types (ASTM D-5986) of various functional groups can also be made. This is particularly important for application to the higher-molecular-weight solid constituents of petroleum (i.e., the asphaltene fraction).

It is also possible to derive structural parameters from infrared spectroscopic data, and these are $\text{H}_\text{S}/\text{C}_\text{S}$, saturated hydrogen to saturated carbon ratios, $\text{C}_\text{P}/\text{C}$, paraffinic character; $\text{C}_\text{N}/\text{C}$, naphthenic character; %Me, methyl content; and $\text{C}_\text{MP}/\text{C}_\text{SU}$, chain length. In conjunction with proton magnetic resonance (see next section), further structural parameters, such as the fraction of saturated methyl groups ($\text{C}_\text{SM}\text{e}/\text{C}_\text{Me}$), can be obtained.

11.3.2. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy has also found considerable use in the structural analysis of petroleum and petroleum products. The technique essentially identifies and counts hydrogen atoms according to their chemical and physical environments (Wen et al., 1978; Dereppe and Moreaux, 1985; Ramaswamy et al., 1986; Gray et al., 1989; Majid et al., 1989). Moreover, proton magnetic resonance

allows rapid and nondestructive determination of the total hydrogen content and distribution of hydrogen among the chemical functional groups present in the sample (Cookson et al., 1986). The technique is also useful as a means of estimating molecular weight (Leon, 1987) and for studying processing effects (Giavarini and Vecchi, 1987).

In the simplest sense, proton magnetic resonance spectroscopy can be used to determine the carbon types (ASTM D-5292, IP 392) and hydrogen content of fuels and other distillates (ASTM D-3701, ASTM D-4808, IP 338, IP 392). However, this chapter is concerned more with the use of nuclear magnetic resonance (^1H and ^{13}C) as a method for structural group analysis.

Early attempts to apply proton magnetic resonance spectroscopy to the study of petroleum showed that hydrogen could be differentiated according to type (Williams, 1959). As a result, structural parameters were estimated for the aromatic systems (Gardner et al., 1959). In addition, it was demonstrated that the information derived by use of proton magnetic resonance was similar to that obtained using other spectroscopic methods (Ramsey et al., 1967).

Thus the nuclear magnetic resonance spectrum of a petroleum fraction can be divided into five major regions, each identifiable with a hydrogen type (Table 11.4). From the areas under each region, it is possible to calculate the fractional distribution of the hydrogen atoms among aromatic hydrogen (H_A) and paraffinic methyl

Table 11.4. General Assignments Used in the Proton Magnetic Resonance Spectra of Petroleum, Heavy Oil, and Bitumen

Symbol	Range τ	Band Center τ	Assignments ^a		
			Major	Minor	
H_A	1.50–3.70	2.60	Aromatic protons		OH in phenols NH in pyrroles
H_α	6.60–8.30	7.45	α -Methyl α -Methylene α -Methine	Paraffinic	
H_N	7.80–8.60	8.20	Methylene Methine <i>cis</i> -Peripheral Bridge Methine	Naphthenic	β -Methyl paraffinic
H_{My}	8.20–9.10	8.65	Methylene other than α - or β -paraffinic		β -Methylparaffinic trans-peripheral bridge methine-naphthenic
H_{Me}	8.60–9.50	9.05	Methyl other than α - or β -paraffinic		trans-Peripheral bridge methine-naphthenic

^aThe letters α and β indicate positions relative to an aromatic ring.

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hydrogen (H_{Mc}). To calculate the average carbon distribution from the hydrogen distribution, it is assumed that H_N , H_{My} , and H_{Mc} are derived from the presence of their respective methylene (CH_2) groups. The principal departure from this assumption occurs in the fused-ring naphthenic contributions to H_{My} and H_{Mc} .

For example, the nuclear magnetic resonance spectrum for the decalin shows that when the bridge hydrogen atoms are on the same side, for example, the *cis* configuration, the entire naphthenic resonance concentrates essentially in a single peak at $J = 8.59$, within the range assigned to H_N . However, when the hydrogen atoms are on opposite sides of the molecule, the *trans* configuration, approximately one-third of the hydrogen signal is located at higher J values, concentrating mainly in the range assigned to H_{Mc} . Thus, H_N may be low by up to 20%.

It is also necessary to assume that each carbon atom attached to an aromatic ring carries two hydrogen atoms. The principal deviation here may be in the lower-boiling fractions, that is, the nonaliphatic material, where substituents on aromatic nuclei may be predominantly methyl groups. An increase in the molecular weight of the fraction is usually accompanied by, among other things, an increase in the size of the alkyl chains attached to an aromatic ring. Hence, the assumption that each benzylic carbon carries two hydrogen atoms may be essentially correct for the higher-boiling fractions that occur in the heavy feedstocks.

Nuclear magnetic resonance has frequently been used for general studies and for structural studies of petroleum constituents (Bouquet and Bailleul, 1982; Hasan et al., 1989). In fact, *proton magnetic resonance (PMR)* studies (along with infrared spectroscopic studies) were perhaps the first studies of the modern era that allowed structural inferences to be made about the polynuclear aromatic systems that occur in the high-molecular-weight constituents of petroleum.

In general, the proton (hydrogen) types in petroleum fractions can be subdivided into three types (Brown and Ladner, 1960) or into five types (Yen and Erdman, 1962). The first approach classifies the hydrogen types into H^*_{ar} , aromatic ring hydrogen; H^*_α , aliphatic hydrogen adjacent to aromatic rings; and H^*_o , aliphatic hydrogen not adjacent to aromatic rings. The second approach subdivided the hydrogen distribution into aromatic hydrogen H_A ($H_A/H = H^*_{ar} = h_a$), α -substituted hydrogen next to aromatics ($H_\alpha/H = H^*_\alpha$), H'' naphthenic hydrogen H_N , methylenic hydrogen H_R , and terminal methyl hydrogen not close to aromatic system H_{Sme} ($H^*_o = H_N/H + H_R/H + H_{Sme}/H$).

Regardless of the method for separating the hydrogen types, the most derived structural parameters take the form of ratios of the various hydrogen types. The H_I/C_A (H_{aru}/C_{ar}) ratio indicates extent of condensation of the unsubstituted aromatic system and the $C_{su}H_I$ (F) ratio gives the degree of substitution. The C_s/C_{su} (n) ratio represents the average chain length, the H_N/C_N ratio is the degree of condensation of naphthenic clusters and f_a is the fraction of carbon that is aromatic. C_A is the total number of aromatic carbon atoms in the sample, R_s is the number of substituted aromatic ring carbons, and R_A is the number of aromatic rings.

After the calculation of the fractional distribution of the protons, the carbon distribution in atoms per molecule may be obtained from the following relationships:

$$C_S = H_T(H_\alpha/2/H_N/2 + H_{My}/2 + H_{Me}/3)$$

$$C_{SA} = H_T \times H_\alpha/2$$

$$C_A = C_T - C_S$$

$$C_P = H_T(H_A + H_\alpha/2)$$

$$C_I = C_A - C_P$$

$$C_{My} = H_T \times H_{My}/2$$

$$C_{Me} = H_T \times H_{Me}/3$$

$$C_N = C_S - (C_{SA} + C_R)$$

$$R_A = (C_I + 2)/2$$

where:

C_S : total saturated carbon atoms per molecule

C_{SA} : total saturated carbon atoms to an aromatic ring

C_A : total aromatic carbons per molecule

C_T : total carbon atoms per molecule from analysis and molecular weight

C_P : peripheral carbon in a condensed aromatic sheet or the total number of hydrogen atoms present if the sheet is completely unsubstituted

C_I : internal carbon in a condensed aromatic sheet

C_{My} : total paraffinic methylene carbon atoms per molecule in locations other than α to an aromatic ring

C_{Me} : total paraffinic methyl carbon atoms per molecule in locations other than α to an aromatic ring

C_N : total naphthenic carbon atoms per molecule

H_T : total hydrogen atoms per molecule from analysis and molecular weight

R_A : aromatic rings per molecule

It is also possible to estimate certain structural parameters for the aromatics within fractions. Thus the ratio C_{SA}/C_P is the average number of carbon atoms directly attached to an aromatic sheet divided by the total peripheral carbon atoms. Expressed in another manner, the ratio C_{SA}/C_P is the degree of substitution of the aromatic sheet. The ratio C_S/C_{SA} is the total number of saturated carbon atoms divided by the number of carbon atoms attached to the edge of the aromatic sheet. Alternatively, the ratio C_S/C_{SA} represents the average number of carbon atoms

attached to a position of the edge of an aromatic sheet. The ratio C_P/C_A is the peripheral carbon atoms per aromatic sheet divided by the total aromatic carbon atoms for that sheet. Alternatively, this ratio is an estimate of the shape of the aromatic sheets; and $(C_S - C_{Me})/C_{Me}$ is the ratio of methylene carbon to methyl carbon, that is, an estimate of the degree of branching in the saturated moieties of the molecule; it also can be written $C_S/C_{Me} - 1$.

The C_P/C_A parameter, which indicates the shape of the aromatic centers of the molecules, is perhaps a little misleading, and literal interpretation can lead to misconceptions about the structures present in, say, residua. It is perhaps more pertinent if this and the other parameters are interpreted on a comparative basis.

On the basis of data derived from proton magnetic resonance investigations, a variety of hypothetical structures have been, and continue to be, proposed for asphaltenes isolated from a variety of crude oils (Winniford and Bersohn, 1962; Yen and Erdman, 1962; Speight, 1970; Ali et al., 1990).

The general indications were that large proportions (up to 50%) of the hydrogen in natural asphaltenes occurred in methylene groups; aliphatic methyl hydrogens were second in abundance, followed by benzylic hydrogens, and, last, the aromatic hydrogens. The relative lack of aromatic and benzylic hydrogen in petroleum asphaltenes appeared to support the occurrence of condensed polynuclear aromatic ring systems. These results also appeared to be in agreement with the kind of structures suggested by Yen and co-workers from their X-ray diffraction studies of asphaltenes (Yen et al., 1961). Hence, it was advocated that asphaltenes are composed of polynuclear aromatic ring systems having 10–20 fused rings bearing aliphatic and naphthenic side chains.

Other workers (Ferris et al., 1966; Speight, 1970) investigated asphaltenes and resins and concluded, by virtue of data derived from proton magnetic resonance spectroscopy (substantiated by electron spin resonance and X-ray diffraction), that the resins contained from 6 to 16 condensed aromatic rings in a single sheet; the latter size appeared to be the maximum condensed structure in asphalt. In the asphaltene molecules, the condensed sheet was repeated one or more times and was linked through saturated chains or rings. The solid-state asphaltenes appeared to form stacks of condensed aromatic sheets that may include individual sheets from several molecules. In benzene, or other effective solvents, the low-molecular-weight stacks appeared to disintegrate to form true solutions, but the higher, less soluble fractions appeared to remain associated.

Application of proton magnetic resonance to the analysis of aromatic fractions from crude petroleum oils and quantitative determinations of the methyl, methylene, and methine carbons in the fractions led to the suggestion that uncertainties existed because of band overlaps occurring in the spectra (Williams and Chamberlain, 1963).

In summary, proton magnetic resonance was one of the first spectroscopic techniques that allowed the derivation of total structural types for asphaltenes.

However, later work has thrown some doubt on the validity of these conclusions; not so much because of the efforts and conclusions of the investigators but more because of the deficiencies of the technique and the potential masking of some of the hydrogen atoms. This has the potential to skew the structural parameters, thereby producing data that are not truly consistent with the molecular types in the asphaltene fraction.

However, it must be recognized that the structural parameters derived by magnetic resonance may present a deceptively simple picture and may be of extremely limited significance for a complex mixture such as the asphaltene fraction.

With the evolution of magnetic resonance and the development of the carbon-13 procedure, further detail has been added to the structure of petroleum fractions that has allowed the more precise identification of carbon atoms in various locations and, hence, a more reasonable calculation of the structural parameters (Severin and Glintzer, 1984; Snape et al., 1984; Michon et al., 1997). However, what is more important, *carbon-13 magnetic resonance (CMR)* can be used to show the differences in carbon distribution of various fraction from different crude oils as well as the carbon distribution in the crude oils themselves.

However, carbon-type analysis does not allow the identification of individual constituents but presents an overall picture of the carbon framework and (if the term can be used without too literal a translation) actually presents an *average* molecular structure of these higher-boiling materials.

The structural details of the carbon backbone obtained from proton spectra are derived by inference, but it must be recognized that protons at peripheral positions can be obscured by intermolecular interactions. This, of course, can cause errors in the ratios that can have a substantial influence on the outcome of the calculations (Ebert et al., 1987). It is in this regard that carbon-13 magnetic resonance (CMR) can play a useful role.

Thus, because carbon magnetic resonance deals with analysis of the carbon distribution types, the obvious structural parameter to be determined is the aromaticity f_a . A direct determination from the various carbon environments is one of the better methods for the determination of aromaticity. Certain regions are often designated for certain types of carbon atoms (Snape et al., 1979): heterocyclic + quinone, 155–160; pyrrole-like, 130–150; mono- to polynuclear aromatic constituents, 120–130; ϵ C, 295; δ C, 29; γ C, 32; β C, 23; and α C, 14.

Through a combination of proton and carbon magnetic resonance techniques, refinements can be made on the structural parameters. However, with the solid-state high-resolution carbon magnetic resonance technique, a number of additional structural parameters can be obtained. For example, quaternary aromatic carbons, tertiary aromatic carbons, the ratio of primary to quaternary aliphatic carbons, and the ratio of secondary to tertiary aliphatic carbons can be estimated (Weinberg et al., 1981).

11.3.3. Mass Spectrometry

Mass spectrometry plays a key role in the identification of the constituents of petroleum and of petroleum products (Aczel, 1979, 1989) (Chapter 7). Mass spectrometric methods are particularly well suited to the analyses of complex mixtures of relatively simple hydrocarbons that comprise the bulk of petroleum and its products.

The principal advantages of mass spectrometric methods are (1) high reproducibility of quantitative analyses; (2) the potential for obtaining detailed data on the individual components and/or carbon number homologues in complex mixtures; and (3) a minimal sample size is required for analysis. The ability of mass spectrometry to identify individual components in complex mixtures is unmatched by any modern analytic technique, an exception perhaps being gas chromatography.

In general, most petroleum samples are very complex mixtures containing literally hundreds and even thousands of individual components. These components tend to form several homologous series of the same general formulae and extend from near-gaseous materials to nonvolatile components. Thus there are disadvantages arising from the use of mass spectrometry: (1) the limitation of the method to organic materials that are volatile and stable at temperatures up to 300°C (570°F); and (2) the difficulty of separating isomers for absolute identification. The sample is usually destroyed, but this is seldom a disadvantage.

The petroleum industry has long been the leader in the use of mass spectroscopy to solve its analytical problems. As soon as instruments became capable of producing repeatable spectra in the early 1940s, hydrocarbon mixtures were analyzed by mass spectrometry with speed and precision not approached by other techniques available at that time. As heat inlet systems evolved, analysis of gases and low-boiling liquids was followed by type analyses of higher-boiling petroleum fractions, and advances in mass-spectroscopic analysis of petroleum and its derivatives paralleled improved instrumentation.

Early work (Lumpkin, 1956) involved development of a procedure for type analysis of the saturate portion of petroleum materials of high molecular weight and employed characteristic fragment masses of paraffins, noncondensed naphthenes, and condensed naphthenes containing two to six condensed rings per molecule to delineate these types. This was followed (Lumpkin, 1964) by an analysis of a trinuclear aromatic portion of a coker gas oil. Six condensed aromatic hydrocarbon types, five sulfur, two oxygen, and one nitrogen compound were identified, and a quantitative analysis based on low-voltage sensitivity showed that alkyl dibenzothiophenes, phenanthrenes, and fluorenes were the major types present.

Other workers (Clerc and O'Neal, 1961) also investigated high-molecular-weight petroleum fractions using a technique developed for examining high-resolution mass spectra of high-molecular-weight solids and concluded that

asphaltic materials consisted principally of condensed ring structures, both aromatic and cyclic, to which one long chain was attached. If two-ring systems were found in a molecule, they were presumably located at opposite ends of a long chain; substitution of the rings was believed to be limited to methyl and ethyl groups. It was postulated that molecules of these types were very probably the principal components of the so-called resin fraction in petroleum and asphalt. Mass spectrometry has also been used to investigate the aromatic structural unit of asphaltenes (Dickie and Yen, 1967) and resins (Dickie and Yen, 1968).

Mass spectrometry can be used readily for the determination of the constituents of gases (ASTM D-2650) or for determining hydrocarbon types in volatile fuels (ASTM D-2425) and in gas oil fractions (ASTM D-2786, ASTM D-3239, ASTM D-5769), but with cautious use a maximum amount of information can be expected. However, heavy oils and residua are for practical purposes beyond the useful range of routine mass spectrometry, but many of the discrete fractions that can now be obtained could be studied qualitatively by high-resolution mass spectral techniques. Many of the higher-molecular-weight constituents in heavy oils and residual are nonvolatile. At elevated temperatures, decomposition could occur in the inlet and any subsequent analysis would be biased to the low-molecular-weight end and to the lower-molecular-weight products produced by thermal decomposition.

Mass spectrometry adds further knowledge to the structural analysis of petroleum by aiding the researcher in the calculation of ring distribution per molecule ions in a mixture. However, there are questions about the application of the technique to the nonvolatile fractions of petroleum. The lack of volatility, which is almost self-explanatory, does not allow accurate identification of the total asphaltene.

The availability of high-resolution instrumentation extends the scope of mass spectrometry for both qualitative and quantitative applications (Altgelt and Boduszynski, 1994). The main advantage of high-resolution techniques is the separation of fragments and molecular ions of the same nominal molecular weight but different elemental composition. In addition, most high-resolution instruments are capable of furnishing precise mass measurements, so that the formulae can be calculated from these measurements.

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

One other point worthy of note is that the py/gc/ms program does not accommodate nitrogen and oxygen species (Chapter 8) whether or not they are associated with aromatic systems. This matter is resolved, in part, not only by the concentration of nitrogen and oxygen in the nonvolatile material (coke) but also by the overall low proportions of these heteroatoms originally present in the asphaltenes. The major drawback to the use of the py/gc/ms technique in study of the aromatic systems in asphaltenes is the amount of material that remains as a nonvolatile residue.

11.3.4. Electron Spin Resonance

Electron spin resonance (ESR) spectrophotometry is useful to supply information supplementary to that obtained by other methods.

The technique provides parameters such as I , the color intensity; g , the Lande g factor; N_g , the spin number; T_1 , the spin-lattice relaxation time; P_C , the population of aromatic carbon per spin; J , the spin-excitation energy; and N_d , the doublet-spin concentration. These parameters give the analytical chemist a look at the electronic configuration of the molecules on a particular fraction, recognizing of course that the parameters will be *averaged* over the *molecular population* of the fraction.

The dark color of the resin fraction and of the asphaltene fraction of petroleum is believed to be closely associated with the organic free radicals, which in turn are usually associated with the aromatic structure (Erdman, 1962). There are also indications that the porphyrins in asphaltenes can be treated as single sheets of alkyl-substituted polynuclear aromatic hydrocarbons, which can be fused to multiple naphthenic rings. Association may also play an important part in the micellar structure of the porphyrins, but it should be remembered that separated porphyrins will behave differently from the porphyrins in petroleum.

The free radical signal can be used as a measure of the asphaltene content of petroleum hydrocarbons. Asphaltenes exhibit a signal equivalent to $2-4 \times 10^{18}$ free radicals per gram, or about 1 per 100 asphaltene molecules, assuming a molecular weight of about 2000 for the asphaltenes (Flinn et al., 1961; Wen et al., 1978; Champagne et al., 1985). The postulate is that the free radicals contribute to the tendency toward micelle formation in the asphaltenes, and these results indicate that the free radical sites were essentially confined to the asphaltene fraction and the resins contain only 2% of the total free radicals present.

11.3.5. Ultraviolet Spectroscopy

Of all of the methods applied to determining the types of aromatic systems in petroleum, one with considerable potential, but that perhaps not fully recognized, is *ultraviolet spectroscopy* (Friedel and Orchin, 1951; Braude and Nachod, 1955;

Rao, 1961; Jaffe and Orchin, 1966; Brown and Searl, 1979; Lee et al., 1981; Bjorseth, 1983).

Ultraviolet spectroscopy can be applied to testing for naphthalene hydrocarbons in aviation fuels (ASTM D-1840) and the evaluation of white mineral oils (ASTM D-2269) as well as testing for the absorbance and absorptivity in petroleum and petroleum products (ASTM D-2008). However, when applied to high-molecular-weight fractions such as asphaltenes, the ultraviolet spectrum typically shows two major regions with very little fine structure. Interpretation of such a spectrum can only be made in general terms (Friedel, 1959; Boyd and Montgomery, 1963; Posadov et al., 1977). More recent studies have shown that the types of chromophores remain constant throughout an asphaltene but the number increases with the molecular weight of the fraction (Yokota et al., 1986).

This technique can add valuable information about the degree of condensation of polycyclic aromatic ring systems when used in conjunction with high-performance liquid chromatography (Chapter 10) (Lee et al., 1981; Bjorseth, 1983; Monin and Pelet, 1983; Felix et al., 1985; Killops and Readman, 1985; Speight, 1986; Yokota et al., 1986; Verhasselt, 1992). Indeed, when this approach is taken, the technique not only confirms the complex nature of the asphaltene fraction but also allows further detailed identifications to be made of the individual functional constituents of asphaltenes.

An asphaltene fraction, produces a multicomponent chromatogram (Fig. 11.10) that differs for each asphaltene sample. In addition, asphaltene subfractions produce a less complex and much narrower chromatograph that may even approximate a single peak that may prove much easier to monitor by the ultraviolet detector. These data provide strong indications of the ring size distribution of the polycyclic aromatic systems in petroleum asphaltenes. For example, from an examination of various functional subfractions, it becomes evident that amphoteric species and basic nitrogen species contain polycyclic aromatic systems having two to six rings per system. On the other hand, acid subfractions (containing phenolic and/or carboxylic functions) and neutral polar subfractions (containing amide and/or imino functions) contain few if any polycyclic aromatic systems having more than three rings per system.

In all cases, the evidence favored the preponderance of the smaller (1–4) ring systems (Speight, 1986), but perhaps what is more important about these investigation is that the data show that asphaltenes are a complex mixture of compound types, which confirms fractionation studies, and, furthermore, the constituents of the asphaltene cannot be represented by any particular formula that is construed to be *average*. Therefore, the concept of a large polycyclic aromatic ring system as the central feature of asphaltene molecules must be abandoned.

The technique is also useful on a before-refining and an after-refining basis. It allows molecular changes in, for example, the asphaltene fraction to be tracked and provides information relative to the chemistry of coke formation.

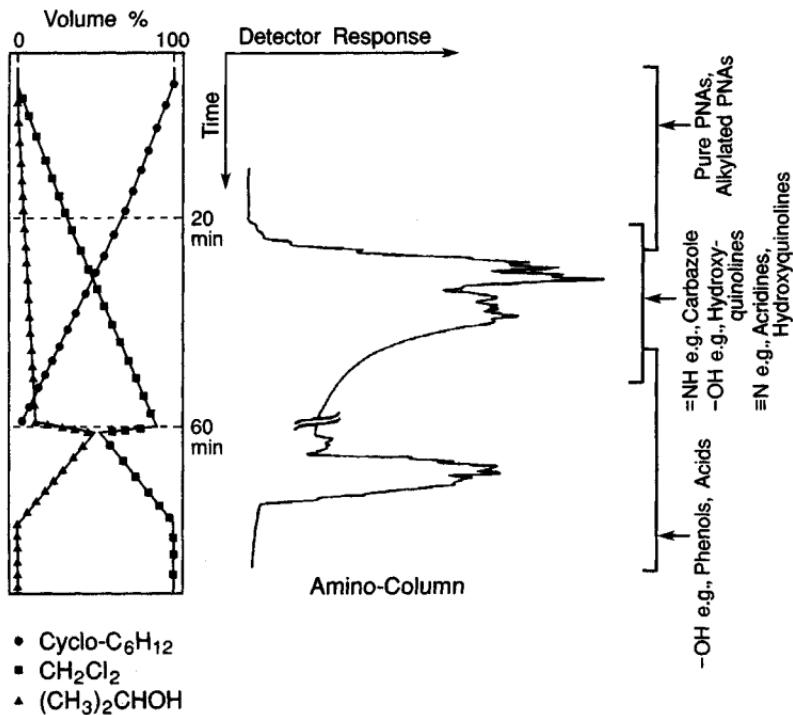


Figure 11.10. HPLC profile of an asphaltene fraction showing the different functional types.

11.3.6. X-Ray Diffraction

The *X-ray diffraction* technique also provides information about the structural qualities of organic materials, but the data provide information about the spatial periodicity within a substance.

Before discussing the main objective of this chapter as it pertains to X-ray diffraction, it must be noted that X-ray methods have become established as a method for the determination of metals in petroleum and petroleum products (ASTM D-4927, ASTM D-5059, IP 352, IP 433).

In terms of structural order, there is one necessary assumption in the application of this method, and it requires that, within a given fraction, the larger portion of the molecules contain within and among themselves certain repeated structural features such as sheets of condensed aromatic rings. Thus, the X-ray diffraction patterns of petroleum fractions are diffuse compared to those of the *well-ordered* carbons, and it is usually very difficult to extract meaningful information from the diffraction patterns.

For materials with limited order, such as pyrolytic carbons, the *X-ray diffraction (XRD)* technique can be used to determine the repeating sequences of the

molecular arrangement. For a dark-colored, solid material in particular, the vectors of the d spacings between 0.5 and 10 Å can be easily derived from a reduced X-ray spectrum. The crystallite parameters often used as structural parameters are (Yen et al., 1961; Yen and Erdman, 1963) L_a , layer diameter; L_c , cluster diameter; d_m interlayer distance; d_γ , inter-chain distance; and M_e , effective layer number. One of the reputed advantages of the X-ray diffraction technique is that it can also be used for a measurement of the aromaticity f_a of the sample. The calculation is based on the relative intensity of the γ band and the (002) band of the pattern.

Early investigations (Nellensteyn, 1938) indicated the presence of a band corresponding to 3.5 C in the X-ray diffraction pattern of an asphaltene fraction and compared the similarity of this feature to that of amorphous carbons, whereas evidence of *crystallinity (molecular order)* in asphaltenes was also indicated (Williford, 1943). Later work (Labout, 1950) showed petroleum asphaltenes to have an X-ray pattern characteristic of amorphous substances.

Use of the well-established Scherrer equation,

$$L = k\lambda/(B \cos \theta)$$

where L is either the crystallite height L_c or the crystallite diameter L_a , B is the half-peak width, θ is one-half of the diffraction angle (2θ), k is a constant (for L_a , $k = 1.00$; for L_c , $k = 1.84$), and λ is the wavelength of the incident beam. This, of course, assumes that asphaltenes have repeating aromatic units with a tendency to stack in layers, as in the case of carbon and graphite. Interlayer distances $c/2$ are calculated from the position of the maximum of the (002) band. The data derived using this equation refer mainly to the structures found in the asphaltene fraction of petroleum. The data indicate that layer diameters L_a are of the order of 6–15 Å, interlayer distances $c/2$ fall into the range 3.5–3.8 Å, and stack heights L_c are about 10–16 Å, which suggests that there are three to five aromatic lamellae per stack.

In addition, the X-ray diffraction patterns of the asphaltene fraction have been used to make estimates of the fraction of aromatic carbon f_a using the relationship

$$\begin{aligned} f_A &= C_{\text{aromatic}}/C_{\text{total}} \\ &= A_{002}/(A_{002} + A_\gamma) \end{aligned}$$

where A represents the areas under the respective peaks.

Other investigations (Young, 1954; Padovani et al., 1959; Bestougeff, 1967; Pollack and Yen, 1969) indicated that the asphaltenes might consist of condensed aromatic sheets carrying naphthenic and paraffinic substituents and could be explained on the basis of polynuclear aromatic sheets of 9–15 Å diameter, spaced about 3.6 Å units apart. A structure consisting of about four sheets could be obtained before the natural heterogeneity of asphaltenes prevented further accumulation.

However, accumulation of other nuclei was still possible because the *asphaltene molecules* were considered to contain two or more polynuclear aromatic sheets sigma-bonded by aliphatic carbon chains. Chain orientation of aliphatic groups, spaced about 5.7 Å apart in the manner of a saturated carbon chain or loose net of naphthenic rings, was also indicated.

X-ray diffraction used at very small angles, *small angle scattering* (SAS), has also been used for the characterization of heavy fractions of petroleum (Pollack and Yen, 1970). The range of small angle scattering is in the molecular dimension from 20 to 2000 Å. Some of the useful parameters are f , structure number; O_r , surface parameter; l , heterogeneity length; l_c , coherence length; and r_M , radius of gyration. There has been serious criticism of the use of the method for determining absolute structural parameters of petroleum materials (Ebert et al., 1984; Ebert, 1990).

Thus, it is not surprising that X-ray diffraction studies have been used in attempts to elucidate the structure of the micelle (Wen et al., 1978). Molecular weight data (Chapter 12) show that asphaltenes associate even in dilute solution and under the conditions often prescribed for determination of molecular weight. This has raised the issue of asphaltene-asphaltene interactions as well as the means by which asphaltenes exist in petroleum.

Small angle X-ray scattering (SANS) has also been used as a means of determining particle size and asphaltene molecular weight (Espinat et al., 1984; Herzog et al., 1988; Storm et al., 1993) and it is interesting to note that the SANS technique gives good agreement with other methods for the molecular weight of the fractions from gel permeation chromatography for the lower-molecular-weight fractions but was unusable for the higher-molecular-weight fractions.

What is perhaps more important from the findings was that the particle size of the asphaltenes was found to increase as a result of deasphalting. This raises the issue of the changes caused to the asphaltene constituents during deasphalting (perhaps analogous to denaturing the protein during the boiling of an egg) (Speight, 1999). Furthermore, questions have been raised as to the validity of the literal interpretations that have been made of the physical character of asphaltenes that have been separated from petroleum. Therefore, deductions about the nature of the micelle, made on the basis of the behavior of separated asphaltenes, are certainly open to question and reinvestigation.

An X-ray technique (Diamond, 1957, 1958, 1959) can be used to estimate the size groups of aromatic lamellae (sheets) that constitute the molecular structure of synthetic carbons, coals, asphaltenes, and the like. After correction for polarization and absorption, 31 evenly spaced intensity values between $S = 0.66$ and 0.96 (where $S = 2 \sin \theta / \lambda$) are treated with Diamond's matrix H_5 . Corrections for Compton scattering due to hetero- (e.g., noncarbon) atoms in the layers are also applied, and a histogram is derived. Each histogram is made up of seven parts showing, from left to right, size groups consisting of nonaromatic material A and aromatic lamellae of varying diameters, 5.8, 8.4, 10.0, 15.0, 20.0, and 20.0 Å. Application of this technique to petroleum asphaltenes showed that the constituents

were inclined to smaller polynuclear aromatic systems rather than the large polynuclear aromatic graphitic sheets that had been postulated up to that time (Speight, 1975).

As an ancillary comment to this section, the results of *small-angle neutron scattering* (SANS) studies (Overfield et al., 1989) have indicated a true molecular weight below 6000 and indications that this decreases with increasing temperature. Such conclusions can benefit the processing of asphaltene-containing crude oil (such as heavy oil) because they offer some insight into structure of the micelle and the behavior of asphaltenes under processing conditions.

Other uses of the X-ray procedure include a test method for sulfur in petroleum products (ASTM D-2622).

11.4. METHODS FOR HETEROATOM SYSTEMS

Although the major focus of spectroscopic techniques appears to have been delineation of the hydrocarbon skeleton of the nonvolatile constituents of petroleum, the failure of the methods to include the heteroatom systems is a major shortcoming of the structural group determination. In many cases, the presence of functional entities in such molecules will seriously affect, and may even dictate, the behavior of the individual constituents. Nevertheless, efforts have also been made to determine the nature and location of the nitrogen, oxygen, and sulfur atoms in the aromatic systems (McKay et al., 1978).

It is, therefore, necessary to make reference to the efforts that have been made to identify the heteroatom groups, and even though nonspectroscopic methods may have been the prime method, spectroscopy may have played a role in confirming the nature of the heteroatom.

11.4.1. Nitrogen

Nitrogen species occur readily in crude oils, and it must be anticipated that similar species will occur within the asphaltenes.

The most widely accepted theory for the origin of petroleum is that it is derived from a biological source material, and this is supported by the presence of porphyrins in petroleum (Speight, 1999 and references cited therein). Porphyrins are assumed to be products from the degradation of chlorophyll. High-resolution mass spectra of porphyrins extracted from several asphaltenes have been examined (Baker, 1966) and shown to contain 7–18 methylene groups per molecule, whereas absorption spectroscopy gave no indication of oxygen functional groups. Further work (Baker et al., 1967) involving an examination of asphaltenes from a variety of crude oils confirmed the presence of cycloalkyl- and alkyl-porphyrins, and the visible spectra were indicative of either incomplete beta-substitution or bridge substitution.

Studies on the disposition of nitrogen in petroleum asphaltenes indicated the existence of nitrogen as various heterocyclic types (Helm et al., 1957; Ball et al., 1959; Clerk and O'Neal, 1961; Nicksic and Jeffries-Harris, 1968; Moschopedis and Speight, 1976b, 1979; Moschopedis et al., 1981; Schmitter et al., 1983; Jacobson and Gray, 1987). Much of the nitrogen is believed to be in aromatic locations (Kirtley et al., 1993). There are also reports in which the organic nitrogen in petroleum asphaltenes has been defined in terms of basic and nonbasic types (Nicksic and Jeffries-Harris, 1968), and there is evidence for the occurrence of carbazole-type nitrogen in asphaltenes (Clerc and O'Neal, 1961; Moschopedis and Speight, 1979).

An analysis of the nitrogen and oxygen compounds from crude oil using high-resolution mass spectrometry as the principal analytical tool showed a variety of compound-types to be present. These included indoles, carbazoles, benzcarbazoles, pyridines, quinolines and higher benzologs, pyridones and quinolones, dibenzofurans, naphthobenzofurans, dinaphthofurans, phenols, carboxylic acids, aliphatic ketones, and esters (Snyder, 1968, 1969).

More recent assumptions include nitrogen in asphaltenes on the basis of not more than one nitrogen atom per molecule (Guiochon, 1982). Such an assumption may be difficult to justify on a natural product basis where molecules with two or more nitrogen atoms are known but it would certainly serve as a reasonable guide for molecular studies where generalizations are often necessary.

Recent studies (Schmitter et al., 1984) have also brought to light the occurrence of four-ring aromatic nitrogen species in petroleum. These findings are of particular interest because they correspond to the ring systems that have been tentatively identified by application of high-performance liquid chromatography to the basic nitrogen fraction of asphaltenes.

Application of X-ray absorption near-edge structure (XANES) spectroscopy to the determination of nitrogen species in asphaltenes confirmed the absence of saturated amines with pyrrole-type nitrogen and pyridine-type nitrogen being the two major types of nitrogen (Mullins, 1995). In fact, the technique showed the predominance of pyrrole-type nitrogen in the samples examined.

There has also been some focus on the metal species in asphaltenes using electron spin resonance (Tynan and Yen, 1969; Shepherd and Graham, 1986). The data indicate that there are, in addition to other metal species, two different types of vanadium, one bound and the other free, occurring naturally in petroleum, both as tetravalent vanadium. It was suggested that the observed vanadium occurring in an asphaltene fraction is associated with the asphaltene molecule itself, most probably the aromatic portion.

11.4.2. Oxygen

Of the heteroatom-containing species in petroleum, there are more data pertaining to the locations of the oxygen atoms than to the sulfur and nitrogen atoms. However,

the majority of the data relates to oxygen functions in blown (oxidized) asphalt and residua that may be of little relevance to the oxygen functions in the native materials.

Infrared spectroscopy has been used to identify various functional groups including hydroxyl (3450 cm^{-1}) and carbonyl ($1695\text{--}1725\text{ cm}^{-1}$) (McKay et al., 1978). In combination with nitrogen titration data (Jacobson and Gray, 1987), better representations of the structural groups can be made. In terms of functional entities in petroleum, one of the most beneficial uses of infrared spectroscopy is in the study of hydrogen bonding in petroleum. It has been shown that phenolic and/or alcoholic hydroxyl and the pyrrole-type imino groups existed largely, and often entirely, as hydrogen-bonded complexes (Petersen, 1967).

Oxygen has been identified in carboxylic, phenolic, and ketonic locations (Nicksic and Jeffries-Harris, 1968; Moschopedis and Speight, 1976a, 1976b; Ritchie et al., 1979a, 1979b) but is not usually regarded as being located primarily in heteroaromatic ring systems. In the context of polyhydroxy aromatic nuclei existing in Athabasca asphaltenes, it is of interest to note that pyrolysis at 800°C (1470°F) results in the formation of resorcinols (Ritchie et al., 1979a), implying that such polyhydroxy aromatic rings systems may indeed exist in the asphaltenes.

An analysis of the nitrogen and oxygen compounds from crude oil using high-resolution mass spectrometry as the principal analytical tool showed a variety of compound-types to be present. These included indoles, carbazoles, benzcarbazoles, pyridines, quinolines and higher benzologs, pyridones and quinolones, dibenzofurans, naphthobenzofurans, dinaphthofurans, phenols, carboxylic acids, aliphatic ketones, and esters (Snyder, 1969).

A very important aspect of the presence of oxygen functional groups is the identification of these functions and definition of their role in determining the physical properties of the system. The physical properties can also influence the structure of the micelle (Moschopedis and Speight, 1976a; Branthaver et al., 1993; Bukka et al., 1993).

For example, derivation of the functional groups using such techniques as silylation of hydroxyls, esterification of acid functions, and quaternarization of amines has been used successfully. Examination of the products from oxidative degradation or hydrogenolysis as well as the products of alkylation, dealkylation, or scission of carbon-nitrogen, carbon-oxygen, or carbon-sulfur bonds are useful methods.

11.4.3. Sulfur

Sulfur occurs in petroleum as benzothiophenes, dibenzothiophenes, and naphthalenebenzothiophenes, and many of these sulfur types occur in the asphaltene fraction (Clerc and O'Neal, 1961; Nicksic and Jeffries-Harris, 1968; Speight and Pancirov, 1984; Ngassoum et al., 1986; Rose and Francisco, 1988). More highly

condensed thiophene types may also occur in the asphaltene fraction but are precluded from identification by low volatility. Other forms of sulfur that occur in asphaltenes include the alkyl-alkyl sulfides, alkyl-aryl sulfides, and aryl-aryl sulfides (Yen, 1974; Waldo et al., 1992).

Application of Fourier transform infrared spectroscopy and sulfur-33 magnetic resonance spectroscopy has provided valuable data about the distribution of the sulfur types in petroleum, particularly the partition of sulfur into aromatic types and aliphatic types (Novelli et al., 1984). It is particularly interesting to note that sulfur exists in a variety of locations that may be dependent on the natural product precursors and the mechanism of maturation.

On a natural product basis, sulfur (as thiophene sulfur) is more difficult to identify. The presence of sulfur, other than the sulfur-containing amino acids cysteine and methionine, is still speculative, although there are means by which inorganic sulfur can be incorporated into petroleum as organic sulfur (Hobson and Pohl, 1973; Orr, 1977; Orr and Sinninghe Damste, 1990).

An interesting aspect of sulfur identification has arisen through the application of X-ray absorption spectroscopy to answer the question about sulfur forms in asphaltenes (George et al., 1990; Kelemen et al., 1990). The data gave a clear demonstration of the existence of nonvolatile sulfide and thiophenic sulfur in the asphaltenes.

Application of XANES spectroscopy to the determination of sulfur species in asphaltenes confirmed the presence of thiophene sulfur and sulfide sulfur (Mullins, 1995). In fact, the technique showed the predominance of thiophene sulfur and, to a lesser extent, sulfide sulfur in the samples examined.

11.4.4. Metals

Questions about the nature of the metal species in petroleum have been ongoing for the past several decades. Metals are important because of the manner in which they can interact with catalysts, causing deactivation of the catalyst and also appearing to promote coke formation.

Metals are not found in any fractions that boil below 540°C (1000°F) (Reynolds, 1998). Typically, the asphaltenes have the highest concentration of vanadium and other metals. Most often, in characterizing metal complexes in crude oils, an asphaltene precipitation is performed that concentrates the vanadium (as well as nickel and iron). The nickel and nitrogen distributions are very similar to the vanadium distributions, in general, with the asphaltene fraction having the highest concentrations. The metals are found bound in two types, *metallo-petroporphyrins* and *metallo-nonporphyrins*. The former have the distinctive ultraviolet-visible Soret band due to the highly conjugated porphyrin ring system, and the latter is comprised of whatever metal concentrations are not accountable by the ultraviolet-visible Soret band.

The different types of metals led to some controversy because only metallo-porphyrins have been unequivocally identified. This had led to many studies over the years that indicated that the metallo-nonporphyrin compounds are vanadium bound with four nitrogen atoms in the first coordination sphere as porphyrins or with other heteroatoms (combinations of nitrogen, sulfur, and oxygen) not in the porphyrin environment.

Metals (i.e., nickel and vanadium) are much more difficult to integrate into the asphaltene system. The nickel and vanadium occur as porphyrins (Baker, 1969; Yen, 1975; Malhotra and Buckmaster, 1985; Shepherd and Graham, 1986), but whether or not these are an integral part of the asphaltene structure is not known. Some of the porphyrins can be isolated as a separate stream from petroleum (Branthaver and Dorrence, 1978; Reynolds et al., 1989; Branthaver, 1990).

Inductively coupled plasma emission spectroscopy has been used for the determination of trace elements in ash residues from various crude oils (Saban et al., 1984). The data were applied to determining the origin and occurrence of crude oils as an aid in oil exploration. Nevertheless, the technique does offer valuable information about the occurrence of trace elements in petroleum.

Inductively coupled plasma emission (ICAP) spectroscopy has also been used, in conjunction with graphite furnace atomic absorption spectroscopy, to investigate the metals types in petroleum, petroleum products, heavy oil, and bitumen (ASTM D-3605, ASTM D-3831, ASTM D-4628, ASTM D-4951, ASTM D-5184, ASTM D-5185, ASTM D-5600, ASTM D-5708, ASTM D-5863, IP 285, IP 288, IP 362, IP 377, IP 413, IP 428, IP 437) (Reynolds et al., 1984, Reynolds, 1998). The data showed that a considerable percentage (50–80%) of the metals in a suite of crude oils existed in the nonporphyrin form. These nonporphyrin metal species were relatively low-molecular-weight (<400) species that were liberated when the tertiary structure of the asphalt material was denatured by extraction.

Application of *X-ray absorption spectroscopy (EXAFS/XANES)* and ultraviolet-visible spectrometric analysis to the issue of the chemical environment of vanadium in various asphaltenes (Goulon et al., 1984) indicated a contradiction in terms of the amount of metals in porphyrins environments and that the conclusions were method dependent.

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CHAPTER

12

MOLECULAR WEIGHT

12.1. INTRODUCTION

The molecular weight of petroleum, heavy oil, and bitumen is important in studies of chemical constitution and chemical reactivity. For example, the molecular weight of any feedstock will give an indication of the amount of hydrogen required to upgrade the feedstock to a particular product or a series of products (Fig. 12.1). In addition, structural group analysis (Chapter 11) of the various fractions often requires molecular weight data as, for instance, in the characterization of the various fractions for insertion into the various indices and correlation formulae (Chapter 11).

As the boiling points of petroleum fractions increase, the complexity of the constituents in these fractions also increases (Fig. 12.2). The high-boiling fractions of petroleum, and these may include *saturated* constituents (*saturates fraction*) and *aromatic* constituents (*aromatics fraction*) (Chapter 9) depending on the *boiling profile* (Chapter 5) of the crude oil, have an extremely complicated composition. In fact, any attempted isolation of individual compounds is a frustrating and impossible task.

For a variety of reasons, of which structural group analysis and process modeling as well as process chemistry are only three, there is a need to determine the molecular weight of either the original feedstock or the feedstock constituent fractions. Various methods are available for molecular weight determination (Speight et al., 1985), some of which are claimed to be satisfactory and others less adequate to the task. However, for those original constituents and products that have little or no volatility, for example, resins and asphaltenes, *vapor pressure osmometry* (VPO) (ASTM D-2503) has been proven to be of considerable value.

The molecular weight and molecular weight distribution have multiple applications in the analysis and characterization of heavy petroleum fractions. Molecular weight may be determined by a number of methods including (1) vapor pressure osmometry (VPO), also called vapor phase osmometry, (2) size exclusion chromatography (SEC), which is still often referred to by its older name, gel permeation chromatography (GPC), and (3) nonfragmenting mass spectrometry, also called parent ion mass spectrometry. Colligative techniques, such as freezing point depression (cryoscopy), commonly used in the past, have essentially been superseded

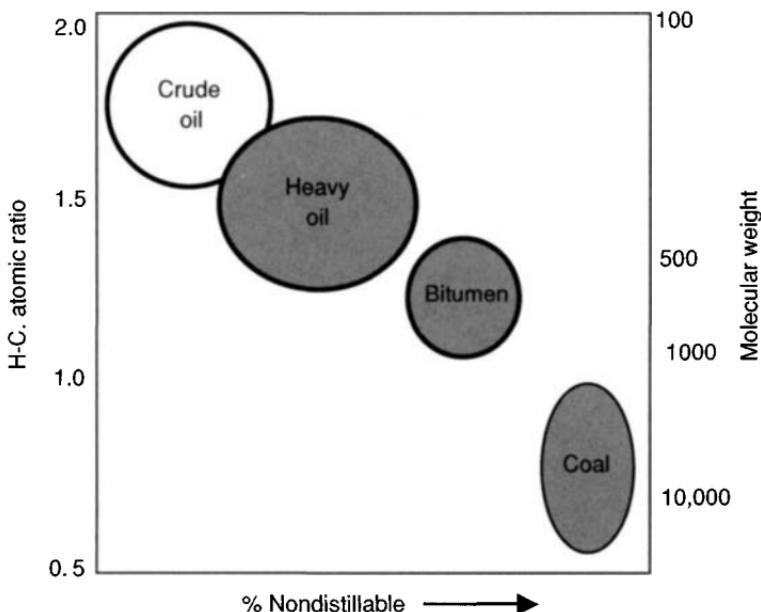


Figure 12.1. Atomic hydrogen-to-carbon ratios of various feedstocks.

by vapor phase osmometry, primarily because the latter is more sensitive and therefore covers a wider molecular weight range.

It is the purpose of this chapter to describe the methods that have been used for determining the molecular weight of petroleum and petroleum fractions without advocating one method over the other. The choice of the method is sample dependent. Differentiation between *particle size* and *molecular weight* is also necessary. In this context of this chapter, a particle may be composed of one or (usually) more molecules, but a molecule is a single entity and is not a particle.

In addition, the molecular weight of a petroleum product appears to be less in demand. Most products, from gasoline to lubricating oil, will be defined by distillation profile or by separation and other physical properties such as viscosity, API gravity, and the like. Therefore, the reader will find that the references in this chapter are devoted to methods designed for determining the molecular weight of the whole feedstock and, to a greater extent, the molecular weight of the various fractions insofar as the data assist in the definition of process chemistry and engineering.

12.2. METHODS FOR MOLECULAR WEIGHT MEASUREMENT

Numerous attempts have been made to measure the molecular weight of petroleum, heavy oil, and bitumen using a variety of different methods, but there is a noticeable

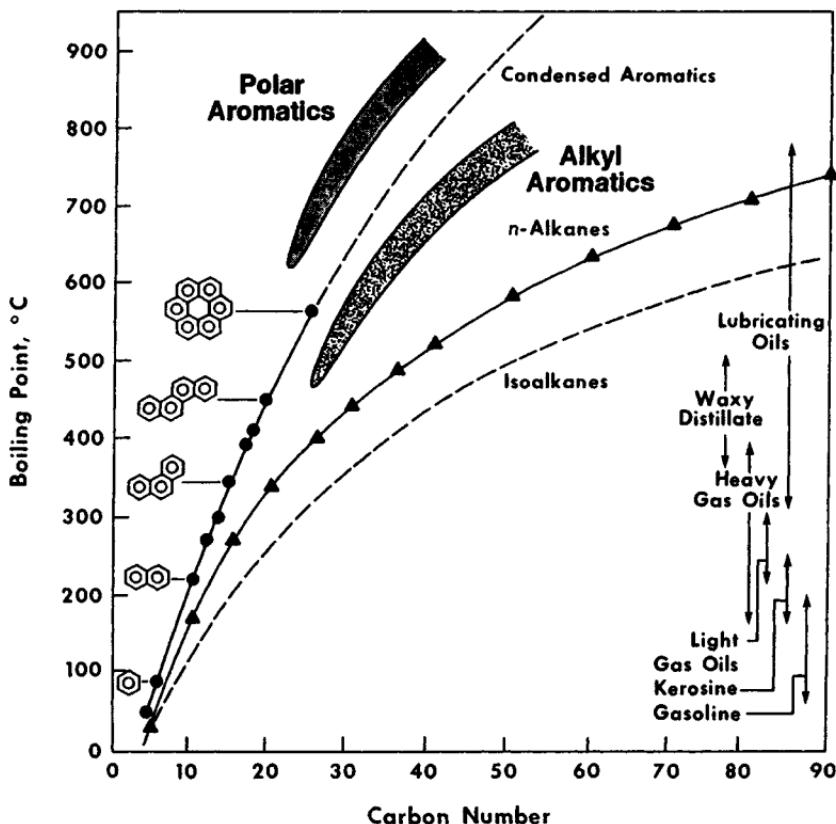


Figure 12.2. Carbon number-boiling point data for pure compounds.

lack of consensus on the value obtained for a specific sample. This has been irreversibly traced to structural aspects of petroleum, heavy oil, and bitumen and, in particular, to the behavior of the asphaltene constituents in molecular dispersion in their own maltenes. In view of the fact that a number of methods used to determine molecular weight information utilize different solvents at different temperatures, the behavior of the component parts such as the resins and the asphaltenes (Chapter 9) in these solvents must be established if a consistent picture of petroleum structure and behavior is to emerge (Chapter 14).

With the goal of structural information, the molecular weight of petroleum fractions has been the subject of much discussion over the past several decades. The reliability of the method, the meaning of the term *average molecular weight*, and the interpretation or usefulness of the data have received considerable attention.

In cases in which only approximate values for molecular weight are required, use can be made of several physical property correlations (Mills et al., 1946; Ali, 1971) that involve correlations such as a molecular weight-boiling point-density

correlation. This correlation is believed to be satisfactory for determining molecular weights in the range of 240–300 for any petroleum fraction for which a good 50% boiling point can be obtained. The viscosity correlation (Hirschler, 1946; Mills et al., 1946) was used for lubricating oil fractions of molecular weight 240–700 using correlations for viscosity with gravity and for viscosity at 37.8°C (100°F) with viscosity at 98.9°C (210°F). However, for more accurate determinations of molecular weight, direct measurement is necessary.

Currently, of the methods available, several standard methods are recognized as being useful for determining of the molecular weight of petroleum fractions and 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.

Methods for molecular weight measurement are also included in other, more comprehensive standards (ASTM D-128, ASTM D-3712), and there are several indirect methods have been proposed for the estimation of molecular weight by correlation with other, more readily measured physical properties. They are satisfactory when dealing with the conventional type of crude oils or their fractions and products and when approximate values are desired.

12.2.1. Vapor Pressure Osmometry

Vapor pressure osmometry (ASTM D-2503), also called vapor phase osmometry, is a relatively simple and cheap method for the determination of molecular weight.

Most osmometers can operate over a range of temperature through the use of probes that cover specific temperature ranges. The method gives the *number average molecular weight* and not the molecular weight distribution.

Vapor pressure osmometry is one of a group of techniques that measure properties based on the number concentration of molecules (i.e., colligative properties). The method measures the degree to which the vapor pressure of a solvent is lowered by the presence of a solute through a temperature effect.

The measuring elements are two temperature-sensitive thermistors placed in a closed, heat-insulated chamber. By means of two syringes, a drop of solvent is placed on one and a drop of the sample in solution in the same solvent is placed on the other. The chamber is saturated with solvent vapor and carefully temperature controlled. Because the solution has a lower vapor pressure than the solvent, solvent from the chamber atmosphere will condense on it. The difference in vapor pressure is proportional to its sample concentration. The heat of condensation warms the solution drop until its vapor pressure is the same as that of the surroundings. From then on, a steady state of condensation and warming is established. The temperature increase is measured and recorded. The solvent drop on the other thermistor is in equilibrium with the solvent in the chamber and, theoretically, gives no temperature effect. In reality, convection and other effects cause minute disturbances in the system, the effect of which can be minimized by subtracting the voltage of the solvent thermistor from that of the solution thermistor.

The temperature difference, ΔT , is related to concentration and molecular weight at infinite dilution by the equation:

$$\Delta T = K_1 c / \text{MW}$$

where K_1 is a constant determined by calibration and c is the solute concentration. The effect is measured at several concentrations, and the results are plotted versus the reciprocal of the molecular weight ($1/\text{MW}$) and extrapolated to zero concentration (also referred to as unlimited dilution).

In the early days of vapor pressure osmometry, ranges of error were accepted or at least recognized that made some of the data questionable. For example, at molecular weight at about or above 5000, the error might be as much as $\pm 10\%$ or even as high as $\pm 15\%$. Modern instruments have reduced experimental errors severalfold by allowing the application of very small and precisely repeatable sample and solvent drops on the thermistor beads. Thus measurements of molecular weight up to about 50,000 are now possible. In addition, samples of much lower concentrations can now be measured, allowing linear extrapolation to zero concentration, in contrast to those from more concentrated solutions.

However, one of the issues that arises through the use of this method for determining the number average molecular weight is that there can be a shift to the

low values by the presence of low-molecular-weight contaminants. For example, traces of the solvent (other than that used for the molecular weight measurement) that remain after the extraction or fractionation process(es). Alternatively, if the sample is an oil fraction, there may be some inclusion of lower-boiling constituents that, by rights, belong in the preceding fraction. Residual toluene may not affect the molecular weight measured in toluene as long as the effect is not due to sample concentration by weight but it would certainly effect the molecular weight as measured in pyridine, nitrobenzene, or in any other solvent with a shift to lower than real values.

A common solvent for vapor pressure osmometry is toluene that is satisfactory for hydrocarbons and moderately polar compounds. However, for the highly polar fractions, such as asphaltenes, more polar solvents such as pyridine are required. The molecular weight of such fractions measured by vapor pressure osmometry in pyridine are distinctly lower than those measured in toluene (Moschopedis et al., 1976; Speight et al., 1985) indicating a lower degree of aggregation, assuming that contamination with trace amounts of previously used solvent in the separation of the samples can truly be excluded.

An aspect of the number average molecular weight by vapor pressure osmometry that also requires consideration is the possibility of some, or even preferential, aggregation of several small polar molecules with a much larger polar molecule during sample collection (precipitation) or during fractionation. The aggregates dissociate in the solvents used for molecular weight measurement, releasing some or all of the low-molecular-weight species. Such aggregation is favored by precipitation of asphaltenes where occlusion of polar molecules from the maltene fraction is common (Ali et al., 1985). However, this effect does not even require contamination with foreign material but is possible in any sample containing highly polar molecules of widely different molecular weights. It slants the resulting number average molecular weight toward low values because the more numerous small molecules dominate over the fewer large ones even though their amounts by weight may be the same or smaller. A number average molecular weight of 5000 thus does not preclude the presence in that fraction of several weight percent of molecules at least 10 times larger, i.e., of around 50,000.

Another potential problem with any molecular weight measurement of asphaltenes is their tendency to become less soluble after isolation. In crude oil and its heavy fractions, the asphaltenes are maintained dispersed in the nonasphaltene material by interaction with the resins (soluble polar molecules) (Chapter 9). However, once they are isolated by precipitation, the asphaltene constituents can be considered to be denatured, analogous to a hard-boiled egg as opposed to a fresh egg. Properties may change and, hence, asphaltenes' solubility can be quite different.

The observance of lower than true molecular weights through the influence of solvent and/or adsorbed lower-molecular-weight species on the asphaltene constituents is not specific to the vapor pressure osmometry method. It applies to

any method producing number average results. Only further fractionation or other suitable measurements can provide the molecular weight distribution of these polar fractions. Re-precipitation or further fractionation of asphaltenes mitigates the preferential solvation of large polar molecules by small ones (Speight et al., 1984).

One technique for reducing the effect of aggregation is to measure the molecular weight of polar species (asphaltenes) at different concentrations and different temperatures to illustrate and negate any aggregation effects. Thus the molecular weight is measured at three different concentrations at each of three different temperatures (Speight, 1994). The data are extrapolated to determine the molecular weight at zero concentration at each temperature, after which they are extrapolated to room temperature to negate concentration and temperature effects. This, of course, assumes that the extrapolation line is straight!

Thus the molecular weight of pentane-asphaltenes measured by vapor pressure osmometry in nitrobenzene are even lower than those reported from measurements in pyridine, with differences ranging from 5 to over 50%. In fact, raising the temperature of the sample chamber (in which the probe is contained) to 100°C (212°F) and above lowered the results by another few percent. Such behavior strongly suggests that even nitrobenzene at the regular vapor pressure osmometer temperature (37.5°C, 100°F) was not sufficient to overcome all the intermolecular aggregation. This not an isolated event but seems to be a common occurrence, because it was observed with pentane-asphaltenes from a wide variety of crude oils.

The *aggregation effect*, which has, on occasion, been incorrectly referred to as an *error*, describes the fact that the accuracy of the molecular weight value is influenced by *aggregation* of the molecular species in solution. In some instances, this may not be classed as an error insofar as the aggregation is recognized and the method is used (along with molecular weight determination in a polar solvent) to determine the maximum aggregation that can occur in the nonpolar solvent. Such effects are magnified when measuring the molecular weight of the asphaltenes that consist primarily of polar (heteroatom) constituents. Indeed, from such experiments the aggregation effect can be determined as the ratio of the molecular weight in a nonpolar solvent (e.g., toluene) to the molecular weight on a polar solvent (e.g., pyridine or nitrobenzene). Thus:

$$\text{aggregation factor } N = \text{MW}_{\text{toluene}} / \text{MW}_{\text{pyridine}}$$

or

$$\text{aggregation factor } N = \text{MW}_{\text{toluene}} / \text{MW}_{\text{nitrobenzene}}$$

Asphaltene constituents naturally aggregate in nonpolar solvents, but it must also be recognized that another possible reason for finding higher molecular weight for asphaltenes is caused by the susceptibility of the polar molecules to oxidation after separation (Moschopedis and Speight, 1978). The inclusion of polar oxygen

functions by oxidation increases the polarity and hence their ability to aggregate. Therefore, storage of the asphaltenes in an inert atmosphere (nitrogen) and in the dark is desirable.

Other solvents such as benzene (now in disfavor because of environmental concerns) have been used, as have a variety of polar solvents. Of the latter, tetrahydrofuran is often cited as a successful solvent. This seemed to arise because of the solubility of coal-derived asphaltenes in tetrahydrofuran. However, coal-derived asphaltenes are the products of thermal processes and bear no relationship to petroleum asphaltenes. Indeed, the use of tetrahydrofuran in the chromatographic separation processes for petroleum (Chapter 10) is to be approached with caution because of the tendency of tetrahydrofuran to react with the adsorbent and form by-products. In a summary of the current context, petroleum asphaltenes often exhibit a somewhat lesser solubility in tetrahydrofuran than in toluene and in pyridine. However, in the darkness of the solution, the insoluble particles may be difficult to detect. Indeed, a similar effect has been noted in pyridine and in *o*-dichlorobenzene as well as in a variety of other (supposedly) good polar solvents. Whatever the solvent of choice, care must be taken to ensure compete solubility of the solute, otherwise anomalous data will be produced that bear little relationship to *accuracy* and *precision*.

As a consequence of the consideration of these effects, a molecular weight of petroleum asphaltenes that is in excess of 2500 is questionable and the true molecular weight is likely to be lower (Speight, 1999).

In the author's experience, pyridine and nitrobenzene have proven to be adequate solvents for molecular weight determination, subject to a thorough premeasurement check showing the lack of any insolubility, and probably provide the best indicator of the aggregation number for asphaltenes.

However, as a final word to this section, caution is advised in the use of nitrobenzene. Raising the temperature when nitrobenzene is used as the solvent is not without some risk. In the author's experience, having the probe fly past one's ear because of the nitrobenzene deciding to expand uncontrollably (explode) under the conditions of the experiment resulting in the probe being launched violently is not for the faint hearted! It can be quite a stimulant (not recommended) to the heart rate!

12.2.2. Freezing Point Depression

Many methods exist for determination of the molecular weight of petroleum fractions (Speight et al., 1985; Speight, 1999 and references cited therein). Most of the early molecular weight determinations on hydrocarbon oils used simple forms of the cryoscopic (freezing point depression) method (ASTM D-2224).

The average molecular weight of petroleum hydrocarbon mixtures is used in characterization and correlation studies (Speight, 1999). Also, molecular weight is used for heat exchange evaluations of distillation columns and for monitoring the progress of cracking processes.

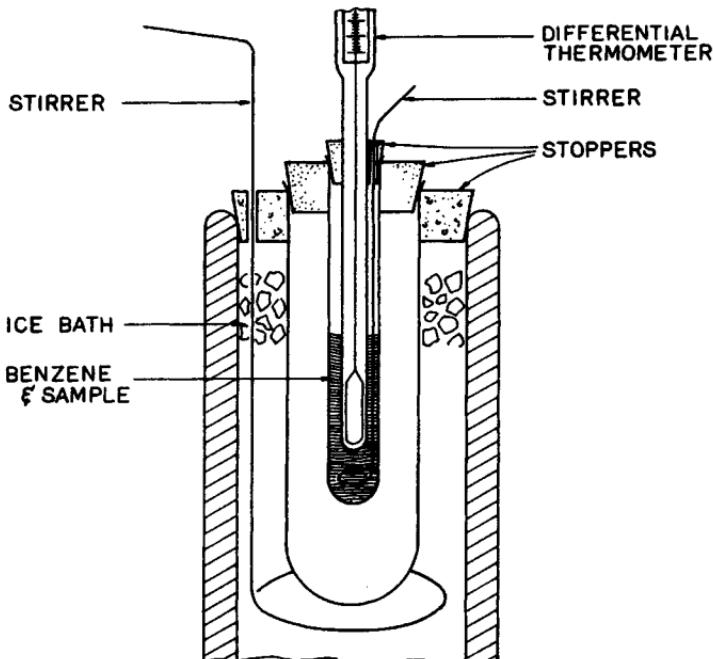


Figure 12.3. Apparatus for molecular weight determination by freezing point depression.

This method using the concept of freezing point depression determines the average molecular weight of various fractions with simple equipment (Fig. 12.3). The samples must be completely soluble and chemically inert in the solvent (benzene). Molecular weight values represent a number-average molecular weight for the sample components.

The freezing points for benzene and for a benzene solution containing a known weight of sample are determined from their cooling curves. From the depression of the freezing point by the sample, the average molecular weight is calculated by application of Raoult's law, which states that the vapor pressure lowering of a solvent is directly proportional to the concentration of the solute:

$$(p_0 - p)/p_0 = n_2/(n_1 + n_2)$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively. Thus, if w_2 g of solute of molecular weight M_2 is dissolved in w_1 g of solvent of molecular weight M_1 , Raoult's law gives:

$$(p_0 - p)/p_0 = (w_2/M_2)/(w_1 M_1 + w_2 M_2)$$

For a dilute solution, n_2 may be neglected in favor of n_1 .

Thus the calculation for molecular weight determination by cryoscopy is:

$$M = [W(K_f - \Delta T)]/(\Delta T S)$$

where M is the number average molecular weight, W is the weight of the sample in grams, K_f is the cryoscopic constant for the solvent (K_f for benzene = 65.6), ΔT is the freezing point depression in °C (i.e., the freezing point of benzene minus the freezing point of the solution), and S is the moles of solvent. Many solvents have been tried, but with the best technique an accuracy of 1–2% is to be considered good.

12.2.3. Boiling Point Elevation

Boiling point elevation (ebullioscopic) methods (Jones and Moote, 1963) are, in general use, more rapid and equally accurate but tend to fall short when applied to the higher molecular weight fractions of petroleum, heavy oil, and bitumen. Molecular weights in the low range (<500) are readily determined by vapor-density methods.

For decades, and even now, of the best-established methods for the determination of the molecular weight of oil fractions boiling above 250°C (480°F) the measurement of boiling point elevation (ebullioscopic method) has been preferred (van Nes and van Westen, 1951).

For any one sample, the boiling point elevation is determined at a series of concentrations of solute. Such determinations were carried out in practice by comparing the boiling point of pure solvent, measured in an ebulliometer, with the boiling points, determined in a second ebulliometer, of a series of solutions prepared by adding successive portions of the sample to the solvent. The first ebulliometer serves as the control experiment.

To determine the ebullioscopic constant K , which depends not only on the solvent used but also to a certain extent on the construction of the apparatus and the procedure followed, a series of determinations is carried out on a pure hydrocarbon

of known molecular weight, preferably of the same order of magnitude as the molecular weight under investigation. The ebullioscopic constant calculated for

where M_n is the number average molecular weight and n_i is the number of molecules having a molecular weight M_i .

12.2.4. Size Exclusion Chromatography

There is a method for determining the molecular weight of petroleum, heavy oil, bitumen, and their constituent fractions using size exclusion (gel permeation) chromatography (ASTM D-3593).

The principle of size exclusion chromatography (Chapter 10) is the exclusion of larger sample molecules from smaller pores in the packing. As a result, larger molecules cannot reside in the entire column volume but are restricted to smaller regions. In the extreme, the largest molecules are restricted to the interstitial volume, that is, the space between particles, whereas the smallest ones can penetrate the entire open column volume, that is, the interstitial and all the pore volume. As a consequence, the large molecules elute first and the smallest ones last.

However, when the samples contain polar functions (as do resin and asphaltenes constituents), two complications can arise:

Solute-solute or solute-solvent interaction can result in the formation of larger particles, and thus part, or all, of the sample elutes earlier than it should.

Adsorption of the solute on the column packing can cause all or part of the solute to elute later than it should.

Adsorption of the solute on the column packing has continued to have an adverse effect on the study of asphaltene molecular weights by this method, and permanent damage to the packing has also been observed (Altgelt and Gouw, 1979). Polynuclear aromatic species have a tendency to adsorb strongly on various adsorbents, but mixed solvents containing small amounts of a strongly polar component, such as pyridine, can help resolve much of the adsorption problem.

For the higher-molecular-weight petroleum fractions, such as asphaltenes, column packings of nominal pore sizes between 50–100 and 5000–10,000 Å are used for complete resolution. The bimodal column combinations give good linear calibration curves, and well-characterized polymer samples as well as narrow polymer fractions, for example, polystyrenes, are available for calibrating column sets across the entire molecular weight range.

However, these polymers are structurally different from petroleum constituents and cannot be directly used for accurate calibration. In fact, petroleum fractions, such as the resin fraction and the asphaltene fraction, differ from polymers in three ways: (1) the hydrocarbon skeletal structure; (2) the polar nature; and (3) the varying composition with molecular weight. Therefore, it is preferable to use a set of *narrow* subfractions obtained by preparative size exclusion chromatography

from the same or a similar petroleum fraction for calibration. Calibration curves obtained by polymers should at least be checked with such subfractions and adjusted as necessary.

However, there are disadvantages in the attempt to establish the correct calibration curve for high-molecular-weight petroleum fractions (Reerink and Lijzenga, 1975). The use of petroleum subfractions can be misleading because they are usually too broad; and in samples with broad distributions, the number average molecular weight may be quite different from the peak molecular weight. Thus a good approximation is a calibration curve based on narrow polystyrene fractions or single compounds and multiplied by a factor of 1.5 across the entire molecular weight range.

Above all, it is important to remember that size exclusion chromatography separates by molar volume rather than by molecular weight. The method will, therefore, differentiate by structure in addition to molecular weight.

Errors may also arise from changes in the response factor with increasing elution volume. The reason is that petroleum components of different molecular weights also have different compositions. Ultraviolet detectors respond primarily to differences in aromaticity and the degree of aromatic ring condensation. Refractive index detectors are affected by color intensity, light scattering by very high-molecular-weight aggregates, and also by the change in composition. All must be given due consideration when data interpretation is undertaken. In solutions of asphaltenes, the molecules are aggregated in clusters but the cluster may dissociate in very dilute solutions where the solvents have a degree of polarity. Thus, using the polar solvent, it may be possible to obtain a true molecular solution, as seems to be the case when nitrobenzene is used for molecular weight determination by vapor pressure osmometry. However, depending on the nature of the asphaltene constituents and the solvent, the dissociation process may not be complete and assumptions of single molecular species may be in error. In addition, the adsorption of the species in the packing must not be underestimated.

In principle, size exclusion chromatography is a very powerful method for separating petroleum fractions by molecular weight. It is used frequently in petroleum analysis despite the components tendency to participate in adsorption and aggregation, and other potential problems.

12.2.5. Mass Spectrometry

Nonfragmenting mass spectrometry is nearly ideal for petroleum distillates. It provides a wealth of detail by giving the hydrocarbon types, the formulae, and the concentration of practically all of the components in a fraction (Chapter 7). From these data, the molecular weight distribution and the number average molecular weight can be obtained.

The main mass spectrometric (MS) methods for high-molecular-weight petroleum fractions are field ionization mass spectrometry (FIMS) and field desorption

mass spectrometry (FDMS). These are also called nonfragmenting methods because they produce the *parent ion spectra* that show only the nonfragmented molecules. However, whether this is true for asphaltenes constituents is still under discussion.

The low volatility of the constituents of the resin fraction and the asphaltene fraction is a major drawback, although application of the technique to those species boiling up to the limit of short-path distillation temperatures, that is, to 705°C (1300°F) might be cited in support of the technique. However, the estimated high boiling range of asphaltene constituents (Chapter 9) may negate application of the technique to these molecular species.

Petroleum fractions typically gave symmetrical mass spectrometric molar mass profile (molecular weight distribution) up to a limit of about 2000. However, the ionization sensitivity changes with molar mass and molecular structure. This *molar mass discrimination* can severely impair the application of mass spectrometry to broad petroleum fractions.

Thus, because of the compositional diversity of the fractions and the differences in ion sensitivity among alkanes, aromatics, and polar compounds, the actual distribution may be quite different from the mass profile. Therefore, symmetry is uncertain and a quantitative evaluation would be very questionable. Indeed, because of volatility constraints, quantitative evaluation of the constituents of an asphaltene fraction would be extremely questionable.

12.2.6. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy has been suggested to be used for measuring molecular weight without the limitations incurred by other methods (see above).

The approach is based on the determination of substituted and total aromatic carbon atoms per molecule. However, just like the nuclear magnetic resonance method for structure determination (Chapter 11), there are many assumptions because of the complex nature of asphaltene samples, and these assumptions are subject to inaccuracy and question. At best, one can hope for minimum and maximum values with a large spread between the minima and the maxima.

It is feared that because of the assumptions, the method becomes little more than optimistic mathematical manipulation.

12.3. MOLECULAR WEIGHTS OF VOLATILE FRACTIONS

Petroleum is not a uniform material because the proportions of the various chemical constituents can vary not only with the location and age of the oil field but also with the depth of the individual well. However, on a molecular basis, petroleum is a complex mixture of hydrocarbons plus organic compounds of sulfur, oxygen,

and nitrogen, as well as compounds containing metallic constituents, particularly vanadium nickel, iron, and copper. The hydrocarbon content may be as high as 97%, for example, in the lighter paraffinic crude oils, or as low as 50% or less as illustrated by the heavier asphaltic crude oils. Nevertheless, crude oils with as little as 50% hydrocarbon components are still assumed to retain most of the essential characteristics of the hydrocarbons.

The molecular weights of the volatile fractions are determined by one of the three methods prescribed for the task. Depending upon the feedstock, the range of molecular weight can vary from approximately 100 to 500. Association effects are minimal and usually do not occur. Thus the molecular weights for volatile fractions as determined are considered to be the true molecular weights of the fractions.

12.4. MOLECULAR WEIGHTS OF NONVOLATILE FRACTIONS

12.4.1. Resins

The molecular weights of resin fractions (Table 12.1) are substantially lower than those of asphaltenes and do not usually vary, except for the limits of experimental error, with the nature of the solvent or the temperature of the determination. It may therefore be presumed that the molecular weights of resins, as determined by various methods, are in fact true molecular weights and that forces that result in intermolecular association contribute very little, if anything, to their magnitude.

12.4.2. Asphaltenes

The asphaltene constituent of a feedstock is primarily responsible for the high degree of variability in measured molecular weights. The polarity, aromaticity and concentration of a given solvent and also the temperature of solution govern association to different degrees in different solvents. In addition, the nature or type of the asphaltene plays a role in determining the degree of association. Consequently, the confidence with which the molecular weight of asphaltenes of a given feedstock can be determined reflects the confidence in the molecular weight of the feedstock, but it does not follow that the asphaltene constituents in their native state in the oil are aggregated to the same degree, if at all, when in their own maltenes.

Addition of extraneous solvents for measurement of molecular weights often initiates the aggregation process. Thus any method of measurement utilizing a solvent medium could potentially result in significant errors in the measured molecular weight of asphaltenes. This dilemma resulted in the application of a considerable research effort to define the structure of whole feedstocks at a molecular

Table 12.1. Elemental Composition of Petroleum Resins

Source	Elemental Composition (wt%)					Molecular Weight, Benzene	Atomic Ratios			
	C	H	O	N	S		H/C	O/C	N/C	S/C
Canada	86.1	11.9	1.1	0.5	0.4	786	1.66	0.009	0.005	0.002
	87.6	10.1	1.2	0.3	0.8	772	1.38	0.010	0.003	0.003
	87.0	11.2	0.9	0.5	0.4	831	1.56	0.007	0.005	0.002
	81.9	11.0	1.5	0.5	5.1	863	1.61	0.013	0.005	0.023
	83.9	10.4	1.0	0.5	4.2	914	1.49	0.009	0.005	0.018
	82.1	10.8	1.4	0.8	4.9	798	1.57	0.012	0.008	0.022
	84.7	11.3	0.8	0.4	2.8	811	1.60	0.007	0.004	0.013
	86.5	11.0	1.2	0.5	0.8	842	1.52	0.010	0.005	0.004
	84.4	10.8	1.1	0.4	3.3	802	1.54	0.010	0.004	0.014
	84.0	10.3	1.1	0.4	4.2	810	1.47	0.010	0.004	0.019
	84.1	10.0	0.8	0.5	4.6	865	1.42	0.007	0.005	0.021
	84.4	10.9	0.7	0.4	3.6	1019	1.54	0.007	0.004	0.016
	83.6	11.8	1.0	0.5	3.1	819	1.69	0.009	0.005	0.015
	84.5	11.6	0.9	0.3	2.7	797	1.65	0.008	0.003	0.012
	85.7	11.3	0.4	0.3	2.3	898	1.58	0.004	0.003	0.010
	86.8	9.7	0.7	0.4	2.4	871	1.36	0.006	0.004	0.010
	86.6	11.5	1.0	0.3	0.6	751	1.60	0.009	0.003	0.003
	85.7	11.5	1.2	0.4	1.2	738	1.61	0.011	0.004	0.005
	85.2	11.0	0.5	0.3	3.0	821	1.55	0.005	0.003	0.013
	85.1	11.1	0.8	0.6	2.4	977	1.56	0.007	0.006	0.011
	87.8	10.3	1.0	0.4	0.5	915	1.41	0.009	0.004	0.002
	86.9	11.5	1.0	0.2	0.4	851	1.58	0.008	0.002	0.002
	87.1	11.6	0.3	0.4	0.6	823	1.60	0.002	0.004	0.003
Iraq	77.5	9.0	3.1	0.3	10.1	—	1.39	0.03	0.003	0.048
	80.4	10.7	2.4	0.7	5.8	—	1.59	0.022	0.007	0.027
Italy	79.8	9.7	7.2	trace	3.3	—	1.46	0.067	—	0.016
Kuwait	83.1	10.2	0.6	0.5	5.6	860	1.47	0.005	0.005	0.025
United States	85.1	9.0	0.7	0.2	5.0	—	1.27	0.006	0.002	0.022
Venezuela	79.6	9.6	—4.5—	—	6.3	—	1.45	—	—	0.030

Source: From Koots, J. A., and J. G. Speight, *Fuel* 1975, 54:182, by permission of the publisher, IPC Business Press Ltd. ©.

level (Chapter 14) and to determine the conditions of measurement necessary to obtain reliable values of molecular weights of different samples.

In fact, determining the molecular weights of asphaltenes is a major issue because the asphaltenes constituents have a low solubility in the liquids often used for determination. Also, adsorbed resins lead to discrepancies in molecular weight determination, and precipitated asphaltenes should be reprecipitated several times before the determination. Thus careful precipitation and careful choice of the

Table 12.2. Methods Used for Measurement of Asphaltene Molecular Weight

Method	Range of Asphaltene Molecular Weights		Investigators
	Determined		
Ultracentrifuge	Up to 300,000		Winniford (1963) Witherspoon (1958) Ray et al. (1957) Wales and van der Waarden (1964)
Osmotic Pressure	80,000		Labout (1950)
Monomolecular Film	80,000 to 140,000		Pfeiffer and Saal (1940)
Ebullioscopy	2,500 to 4,000		Griffin et al. (1958) Jones and Moote (1963)
Cryoscopy	600 to 6,000		Labout (1950) Sakhanov and Vassilieu (1927) Katz (1934) Hillman and Barnett (1937) Grader (1942)
Viscometry	900 to 7,000		Wales and van der Waarden (1964) Mack (1932) Erkert and Weetman (1947) Fischer and Schram (1959) Girdler (1965) Reerink (1973)
Light Absorption Coefficient	1,000 to 4,000		Markhasin et al. (1969)
Vapor Pressure Osmometry	1,000 to 5,000		Neumann and Bellstedt (1966) Altgelt (1968) Dickson et al. (1969) Koots and Speight (1975) Suzuki et al. (1982)
Equal Osmotic Pressure	2,000 to 3,000		Kirby (1943)
Equal Vapor Pressure	2,000 to 3,000		Lever (1934)

determination method are both very important for obtaining meaningful results (Speight et al., 1985).

A fairly comprehensive review (Table 12.2; Moschopedis et al., 1976) followed by a study of asphaltene molecular weights by vapor pressure osmometry has been reported and shows that the molecular weights of various asphaltenes are dependent not only on the nature of the solvent but also on the solution temperature at which the determinations were performed (Table 12.3; Moschopedis and

Table 12.3. Molecular Weights of Asphaltenes Using Vapor Pressure Osmometry

Sample Era	Molecular Weight						
	C ₆ H ₆ 37 ^a	CH ₂ Br ₂ 37 ^a	C ₅ H ₅ N 37 ^a	C ₆ H ₅ NO ₂			
				37 ^b	100 ^a	115 ^a	130 ^a
Upper Cretaceous	2092	2010	2103	2000	1990	2050	1940
Lower Cretaceous	4850	3430	2655	2050	1890	1820	1825
	6669	4719	4221	3590	2470	2220	1920
	6415	4562	2687	1650	1550	1410	1500
	5768	4952	2736	2040	2020	1970	2060
	3977	3456	2400	2150	1860	1740	1660
	3782	3483	2829	2350	2030	1900	1990
	4904	4068	2551	2070	1790	1700	1630
	6583	5512	3179	1300	1250	1260	1220
	5886	4589	2439	1830	1700	1670	1650
Carboniferous	4766	3907	2721	2010	1880	1870	1830
	6672	3999	2898	2500	2250	2370	1960
	4174	3667	2683	2170	2090	2140	2160
Lower Devonian	4125	3864	2541	1900	1830	1890	1810

^aSolvent temperature (°C). ^bExtrapolated value.Source: Reproduced from Moschopedis, S. E., J. F. Fryer, and J. G. Speight, *Fuel* 1976, 55:228, by permission of the publisher, IPC Business Press Ltd. ©.

Speight, 1976a; Moschopedis et al., 1976). Data from later work involving molecular weight determinations by the cryoscopic method (Speight and Moschopedis, 1977), however, indicate that the molecular nature of asphaltenes is not conducive to the determination of absolute molecular weights by any one method.

Indeed, for any one particular method, the observed molecular weights suggest that asphaltenes form molecular aggregates, even in dilute solution (Moschopedis et al., 1976), and this association is influenced by solvent polarity, asphaltene concentration, and the temperature of the determination (Figs. 12.4 and 12.5; Speight and Moschopedis, 1977; Speight et al., 1985; Speight, 1999). In fact, it is strongly recommended that, to negate the concentration effects and the temperature effects, the molecular weight determinations be carried out at each of three different concentrations at each of three different temperatures. The data for each temperature are then extrapolated to room temperature (Fig. 12.5).

Thus the molecular weights of asphaltenes span a wide range from a few hundred to several million, leading to speculation about self-association (Sakhanov and Vassiliev, 1927; Mack, 1932; Katz, 1934; Lerer, 1934; Hillman and Barnett, 1937; Pfeiffer and Saal, 1940; Grader, 1942; Kirby, 1943; Labout, 1950; Ray et al., 1957; Griffin et al., 1959; Winniford, 1963; Wales and van der Waarden, 1964; Altgelt,

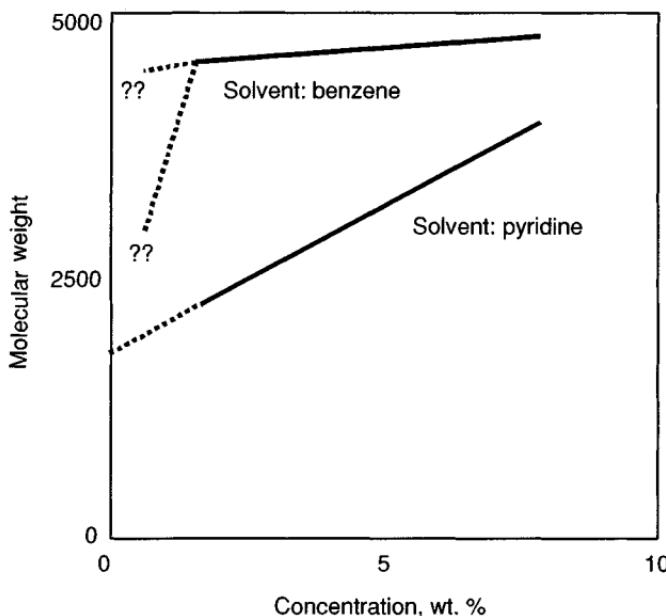


Figure 12.4. Variation of asphaltene molecular weight with concentration and solvent.

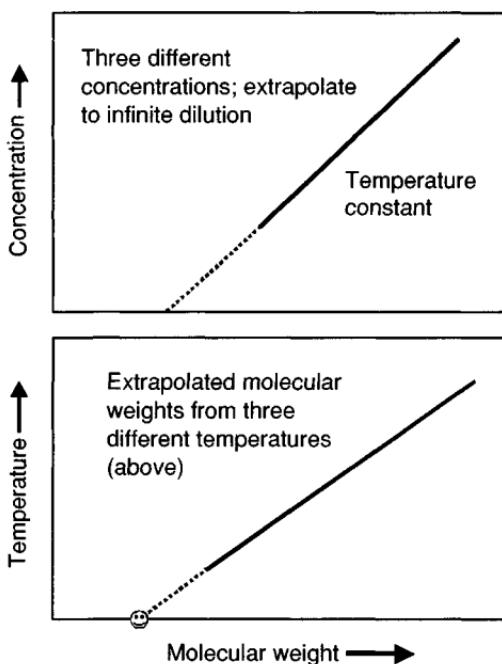


Figure 12.5. Method for negating aggregation effect through concentration and temperature studies in the determination of asphaltene molecular weight.

1968; Markhasin et al., 1969; Reerink, 1973; Koots and Speight, 1975; Speight et al., 1985).

The tendency of the asphaltenes to form aggregates in hydrocarbon solution is one of their most characteristic features and complicates the determination of molecular weight (Winniford, 1963; Speight and Moschopedis, 1977). The average molecular weights measured by means of vapor pressure osmometry (VPO) or size exclusion chromatography (SEC) are significantly influenced by the conditions of the analysis (temperature, asphaltene concentration, solvent polarity) (Altgelt, 1968; Moschopedis et al., 1976; Speight and Moschopedis, 1980; Speight, 1981; Speight et al., 1985; Acevedo et al., 1992). For this reason, molecular weights are reported in the literature as relative values only, and these values may be quite different from the molecular weights of unassociated molecules.

The influence of the asphaltene concentration on the values of molecular weight measured is significant, and it is important to use as high a dilution as possible to measure a molecular weight that at least approaches that of the unassociated asphaltene molecules, remembering that the asphaltene fraction is a complex mixture of different species and that any molecular weight of unassociated species will be an average molecular weight of different chemical species.

The existence of asphaltenes aggregates in hydrocarbon solvents has been demonstrated by means of small-angle neutron scattering (SANS) studies. The physical dimensions and shape of the aggregates are functions of the solvent used and the temperature of the investigation (Ravey et al., 1988; Overfield et al. 1989; Thiagarajan et al., 1995). In addition, surface tension measurements have been used to study the self-association of asphaltenes in pyridine and nitrobenzene (Sheu et al., 1992). A discontinuous transition in the surface tension as a function of asphaltene concentration was interpreted as the critical asphaltene concentration above which self-association occurs.

The study of asphaltene molecular weights by vapor pressure osmometry shows that the molecular weights of various asphaltenes are dependent not only on the nature of the solvent but also on the solute concentration (Fig. 12.4) and the solution temperature at which the determinations were performed (Table 12.4; Moschopedis et al., 1976; Speight, 1987, 1994, 1999). However, data from later work involving molecular weight determinations by the cryoscopic method (Speight and Moschopedis, 1977) indicate that the molecular nature of asphaltenes is not conducive to the determination of absolute molecular weights by any one method.

For any one method, the observed molecular weights suggest that asphaltenes form molecular aggregates, even in dilute solution, and this association is influenced by solvent polarity, asphaltene concentration, and the temperature at which the determination is made. The precise mechanism of the association has not been conclusively established, but hydrogen bonding and the formation of charge-transfer complexes have been cited as responsible for intermolecular association (Yen, 1974). In fact, intermolecular hydrogen bonding could be involved

Table 12.4. Variation of Asphaltene Molecular Weight with Solvent

Asphaltenes	Wt%	Solvent ^a			
		C ₆ H ₆	CH ₂ Br ₂	C ₅ H ₅ N	C ₆ H ₅ NO ₂ ^b
Pentane	100	4050	2730	2310	1610
Reprecipitated ($\times 1$)	93	5120	3380	2590	2010
Resin (C ₅ solubles)	7	710			
Reprecipitated ($\times 3$)	89	8710	5810	—	2640
Resin (C ₅ solubles)	13	797			
Pentane extracted	90	8450	6740		2820
Resin (C ₅ solubles)	10	845			
Heptane	100	6850	4320	3580	2670
Reprecipitated ($\times 3$)	92	8560	6890	4310	2880
Resin (C ₇ solubles)	8	1050			

^a Asphaltene concentration: 2.5% wt/wt; temperature 37°C. ^b Extrapolated values from data derived at 100, 115, and 130°C.

in asphaltene association and may have a significant effect on observed molecular weights (Moschopedis and Speight, 1976b; Speight, 1994, 1999). Indeed, such bonds are known to exist in natural product systems, and they confer stability on various conformational structures (Lewin, 1997).

It is also interesting to note that use of a solvent of low dielectric constant (benzene) does not cause any variation in the molecular weight when the concentration of the asphaltenes (Fig. 12.4) is varied over the range 2–7%. However, use of a solvent of higher dielectric constant (pyridine) caused significant variation in the observed molecular weights over this particular range. Molecular weight determinations at lower (<2%) and higher (>8%) concentrations are subject to instrument sensitivity and solubility interference, respectively. Extrapolation of the pyridine data to infinite dilution, when asphaltene-asphaltene interaction may be assumed negligible, affords molecular weights of the same order (around 1800) as those recorded using nitrobenzene as the solvent. On the other hand, extrapolation of the pyridine data to higher concentrations suggests that molecular weights of the order of those recorded in a solvent of lower dielectric constant (e.g., benzene) may be obtained.

The higher molecular weights recorded when solvents of low polarity are used are undoubtedly the result of intermolecular association between the asphaltene nuclei, but solvents of high dielectric constant are able to bring about dissociation of these asphaltene agglomerations to what, in fact, appear to be single asphaltene particles. Furthermore, this observation precludes asphaltene structures that invoke the concept of a polymer molecule to account for the high molecular weights observed in nonpolar solvents.

Data from a series of asphaltene molecular weight determinations (Table 12.4) present strong evidence to support the contention that *resin* constituents (i.e., precipitant-soluble material) are occluded within the asphaltene matrix during the precipitation procedure. In each case, removal of the resin constituents gives rise to higher observed molecular weights of the *purified* asphaltenes. In addition, and as noted previously for the whole asphaltenes (Moschopedis et al., 1976), the molecular weights of the purified asphaltenes also varied with the solvent used for the determination; that is, solvents of high dielectric constant decrease the observed molecular weights. Furthermore, when the freshly precipitated asphaltenes were extracted continuously (Soxhlet) with different solvents and molecular weight determinations were carried out on the insoluble material, a decrease in the asphaltene molecular weight with the dielectric constant of the solvent was also noted (Table 12.5).

It is of interest to speculate at this point about the means by which the resin material is retained by the asphaltenes. For example, asphaltenes and resins have been suggested to have points of structural similarity (Koots and Speight, 1975; Moschopedis and Speight, 1976a; Speight, 1999) that is responsible for their affinity to each other in solution and in petroleum. As noted above, in the case of

Table 12.5. Variation of Asphaltene Molecular Weight with Extraction

Asphaltenes	Wt%	Solvent ^a			
		C ₆ H ₆	CH ₂ Br ₂	C ₅ H ₅ N ₅	C ₆ H ₅ NO ₂ ^b
Untreated	100	4,050	2730	2,310	1610
Pentane extracted	90	8,450	6740		2820
Extract	10	845			
Heptane extracted	72	8,940	7120	4,380	2980
Extract	28	2,310			
Hexadecane extracted ^c	58	12,490	8800		3510
Extract	42	2,530			
Methyl ethyl ketone extracted	93	15,650		5,980	3060
Extract	7	983			
3-Pentanone extracted	65	18,000		12,410	6380
Extract	35	1,352			
Ether extracted	93	11,370	8730		2910
Extract	7	1,822			
Ethyl acetate extracted	95	12,000	8260	4,270	2880
Extract	5	728			

^aAsphaltene concentration: 2.5% wt/wt; temperature 37°C. ^bExtrapolated values from data derived at 100, 115, and 130°C. ^cStirred at 85°C for 24 h; insolubles separated by filtration; solubles separated by removal of the solvent in vacuo.

Table 12.6. Variation of Asphaltene Molecular Weight with Dispersing Solvent

Solvent	Precipitant	Asphaltene ^a Molecular Weight
Benzene	<i>n</i> -Pentane	5120
Carbon tetrachloride	<i>n</i> -Pentane	5080
Tetrahydrofuran	<i>n</i> -Pentane	8840
Pyridine	<i>n</i> -Pentane	13,390

^aReprecipitated once from the solvent used for the initial precipitation.

amphoteric species, there is potential for strong bonding to occur (Speight, 1994, 1999), thereby increasing the intensity by which the resins are held to the asphaltenes and, also, by which the asphaltene molecules associate with each other thereby requiring stronger dispersing solvents to release the resins (Table 12.6).

Thus the amount of resin may have some influence on the asphaltene yield (and, therefore, on an estimation of crude oil composition); the resin occluded within (or adsorbed onto) the asphaltene during the separation procedure has a considerable effect on the observed molecular weight and, presumably, on the degree of association of the asphaltenes. Indeed, the speculative concept that asphaltenes release the final vestiges of this resin only on swelling by a solvent such as pyridine is also worthy of consideration.

Thus the tendency of asphaltenes to undergo association and/or dissociation depending on the nature of the solvent also appears true for the series of higher-molecular-weight fractions. However, it should be noted here that although the results with asphaltenes available from several crude oils (Moschopedis et al., 1976) suggest that molecular weight varies with the dielectric constant of the solvent, there may be other factors that may in part also be responsible for this phenomenon. The final phenomenon that influences the molecular weight of the asphaltene is the relative polarity of the solvent used in the precipitation technique (Table 12.6).

A particularly appropriate method involves the use of different solvents (at least two), and the data are then extrapolated to infinite dilution (Schwager et al., 1977, 1979). There has also been the use of different temperatures for a particular solvent after which the data are extrapolated to room temperature (Speight et al., 1985; Speight, 1987). In this manner, different solvents are used and the molecular weight of a petroleum fraction (particularly the asphaltenes) can be determined, for which it can be assumed that there is little or no influence from any intermolecular forces. In summary, the molecular weight may be as close to the real value as possible.

In fact, it is strongly recommended that to negate concentration effects and temperature effects the molecular weight determination be carried out at three different concentrations at three different temperatures. The data for each temperature are

then extrapolated to zero concentration and the zero concentration data at each temperature are then extrapolated to room temperature (Speight, 1987).

It is of interest to speculate at this point about the means by which the resin material is retained by the asphaltenes. For example, asphaltenes may be analogous to coal insofar as it appears that asphaltenes have adsorption characteristics and may even exhibit a distinct physical structure or participate in clathrate systems. If this is the case, swelling by a solvent such as pyridine would undoubtedly free resin material from the asphaltenes. On the other hand, if the resin material is retained purely by a surface adsorption phenomenon, it may be expected to be removed from the asphaltenes by the repetitive precipitation. Both effects could play a part in the retention of resin (i.e., precipitant soluble) material by the asphaltenes.

Obviously, many other facets of asphaltene precipitation need to be investigated, but it is obvious from these data that it is extremely difficult to obtain *clean* (resin free) asphaltenes without a multiple-precipitation technique. The amount of resin may have some influence on the asphaltene yield (and, therefore, on an estimation of crude oil composition). However, the resin occluded within (or adsorbed onto) the asphaltene during the separation procedure has a considerable effect on the observed molecular weight and, presumably, on the degree of association of the asphaltenes. Indeed, the speculative concept that asphaltenes release the final vestiges of this resin only upon swelling by a solvent such as pyridine is also worthy of consideration.

Attention should be focused on the delineation of various structural types in the asphaltenes. Because petroleum is actually a continuum of structural types, there is little to be inferred from this study other than the influence of degree of association or on the degree of polymerization (for those concepts based on the concept of a polymer structure).

If, however, the structural types vary from the resins to the asphaltenes, it may be necessary to reassess the concepts of molecular types that have been proposed heretofore. In addition, the concept that the resins may be entrapped within the asphaltene matrix (and may even be analogous to a clathrate compound) warrants further investigation.

It is worthy of mention at this point, because the theory of the physical structure of petroleum is based on the results of the method, that the specific viscosity of asphaltene solutions has also been used to determine asphaltene molecular weights (ASTM D-2502).

The method essentially requires a determination of the relative viscosity n_r , of known solute-solvent systems, when the constant k is derived by the relationship

$$\log n_r = ckM$$

where c = concentration (g per 100 ml) and M = molecular weight. Thus subsequent application of the relationship to solute-solvent systems involving asphaltenes and maltenes allowed Mack, in 1932, to derive molecular weights of the

order of 5000 at 0°C (32°F) to 1800 at 120°C (250°F). Thus it is not surprising that the postulate of the existence of asphaltene clusters within the maltenes evolved and has persisted to the present time.

Application of this procedure to systems involving Athabasca asphaltenes allows derivation of values for the constant k , but transposition of k from one solute-solvent system to another gives inconsistent results. For example, the constants derived from naphthalene-benzene or biphenyl-benzene systems give unexpectedly low molecular weights when applied to asphaltene-benzene systems. Indeed, application of these constants to petrolene-solute systems gives molecular weights of naphthalene and biphenyl in error by some several hundred percent.

Application of the constant k for the biphenyl-benzene system to the asphaltene-petrolene system gives molecule weights within an *acceptable* range. However, the validity is suspect because of the unsatisfactory results obtained when the constants from one solute-solvent system are transposed to a different solute solvent system in which the molecular weight of the solute is known. This is emphasized to an even greater extent by application of the constant derived from the asphaltene-benzene system to the asphaltene-petrolene system, which yields molecular weights of the order of 17,000–60,000.

In view of these inconsistencies, the viscosity method of determining asphaltene molecular weights must be regarded as suspect when the constants k , as derived for one solute-solvent system, are applied to a completely different solute-solvent system. Indeed, Mack's original work involved transposition of data from earlier work by Kendall and Monroe in 1917 and must be regarded as questionable, because these authors considered their own results to be indecisive because data from different solvent systems containing the same solute were in conflict. Even though preliminary application of some of the viscosity data yields asphaltene molecular weights within an acceptable range, the remaining data indicate several inconsistencies in the method, and recognition of this causes some revision of previous theories of the physical structure of crude oil.

In summary, asphaltene molecular weights are variable (Yen, 1974; Speight et al., 1985), there being a tendency to associate even in dilute solution in nonpolar solvents. However, data obtained using highly polar solvents indicate that the molecular weights, in solvents that prevent association, usually fall in the range 2000 ± 500 . There is some support for this conclusion from mass spectrometry studies (Storm et al., 1990), but caution is advised when using mass spectrometry especially where the volatility of the sample is critical to the conclusions. Failure to recover all of the material and the formation of a thermal residue in the system (Speight and Pancirov, 1984) can remove not only the more polar species but also the higher-molecular-weight species.

In view of the potential changes that the asphaltenes of a given feedstock can undergo when diluted with solvents, it is evident that the method used to measure the molecular weight can have a strong bearing on the value obtained. Molecular

weight determinations by vapor pressure osmometry using benzene or toluene as a solvent are likely to be high, principally because of asphaltene associations. It has also been indicated (Mack, 1964) that the values obtained using the cryoscopic method with benzene would yield high values of molecular weight for similar reasons. Because the solubility of asphaltenes in a given solvent increases with an increase in temperature, and indeed asphaltene associations are reduced, it has also been suggested (Mack, 1964) that methods utilizing higher temperatures will yield molecular weights that are more representative. Thus ebullioscopic methods with benzene or cryoscopic methods with camphor or naphthalene as solvents might be the preferred method of molecular weight determination for individual fractions and for whole feedstocks.

12.4.3. Carbenes and Carboids

By definition, *carbenes* and *carboids* are the components of petroleum that are less soluble than the asphaltenes (Fig. 12.6; Chapter 9; Speight, 1999). In fact, carbenes and carboids are regarded as the products of thermal treatment of petroleum, heavy oil, and bitumen. In this sense, molecular weight data have proved helpful in determining the course of the thermal reaction.

For many decades, carbenes and carboids were regarded as the product formed by polymerization and condensation of asphaltene moieties and were, in fact the precursors to coke. It is the initial fragmentation of the asphaltenes that produces the carbenes and carboids (Speight, 1987, 1994). Indeed, where solubility in pyridine is possible (carbenes) molecular weight data show that the carbenes have a lower molecular weight than the respective parent asphaltenes (Table 12.7). It is the relative insolubility of the carbenes and the carboids in the changing oil medium that causes separation as a solid phase and that is the true onset of coke formation.

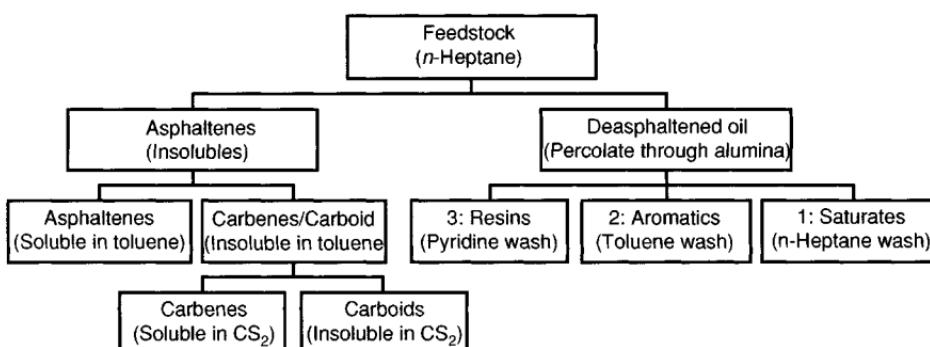


Figure 12.6. Fractionation scheme for feedstocks showing the position of carbenes and carboids.

**Table 12.7. Molecular Weights and Atomic H-C Ratios
for Carbene (Toluene Insoluble/Pyridine Soluble)
Products from the Thermal Decomposition
of Asphaltenes**

Temperature (°C)	H/C Atomic	C_A^a	Molecular Weight
Untreated	1.237	0.45	1890
300	1.114	0.52	1700
350	1.109	0.55	1650
400	1.009	0.61	1580
500	0.987	0.66	1610
600	0.913	0.70	1640

^aFraction of carbon in aromatic locations as deduced by ¹³C NMR.

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CHAPTER

13

INSTABILITY AND INCOMPATIBILITY

13.1. INTRODUCTION

The study of the analysis of crude oil and crude oil products would not be complete without some attention to their stability and incompatibility. Both result in formation of degradation products or other undesirable changes in the original properties of petroleum products, and the analytical methods that provide the data point to the reason for problems in the refinery or for the failure of products to meet specifications and to perform as desired.

Petroleum and its products have been in use for over 5000 years (page 11) (Abraham, 1945; Forbes, 1958a, 1958b, 1959; James and Thorpe, 1994). However, the evolution of the petroleum industry has been accompanied, or driven, by the development of many other products, and the complexities of product composition have matched the evolution of the products (Hoffman, 1992). In fact, it is the complexity of product composition that has served the industry well and, at the same time, had an adverse effect on product use. Product complexity has made the petroleum industry unique among industries.

Current refineries (Fig. 13.1) are a complex series of manufacturing plants that can be subdivided into (1) separation processes, (2) conversion processes, and (3) finishing processes. Incompatibility can occur many of these processes, and the product can also exhibit incompatibility and instability (Por, 1992; Mushrush and Speight, 1995; Speight, 1999).

Product complexity and the means by which petroleum products are evaluated have made the petroleum industry unique among industries. However, product complexity has also brought to the fore issues such as *instability* and *incompatibility*. Product complexity becomes even more disadvantageous when various fractions from different types of crude oil are blended or are allowed to remain under conditions of storage (before use) and a distinct phase separates from the bulk product. The adverse implications of this for refining the fractions to salable products increase (Batts and Fathoni, 1991; Mushrush and Speight, 1995).

The phenomenon of the instability and incompatibility of petroleum products is invariably associated with the chemical composition and physical relationships of the components (Mushrush and Speight, 1995). In most cases, a certain component in one of the fuels reacts with another component in the fuel with which it is

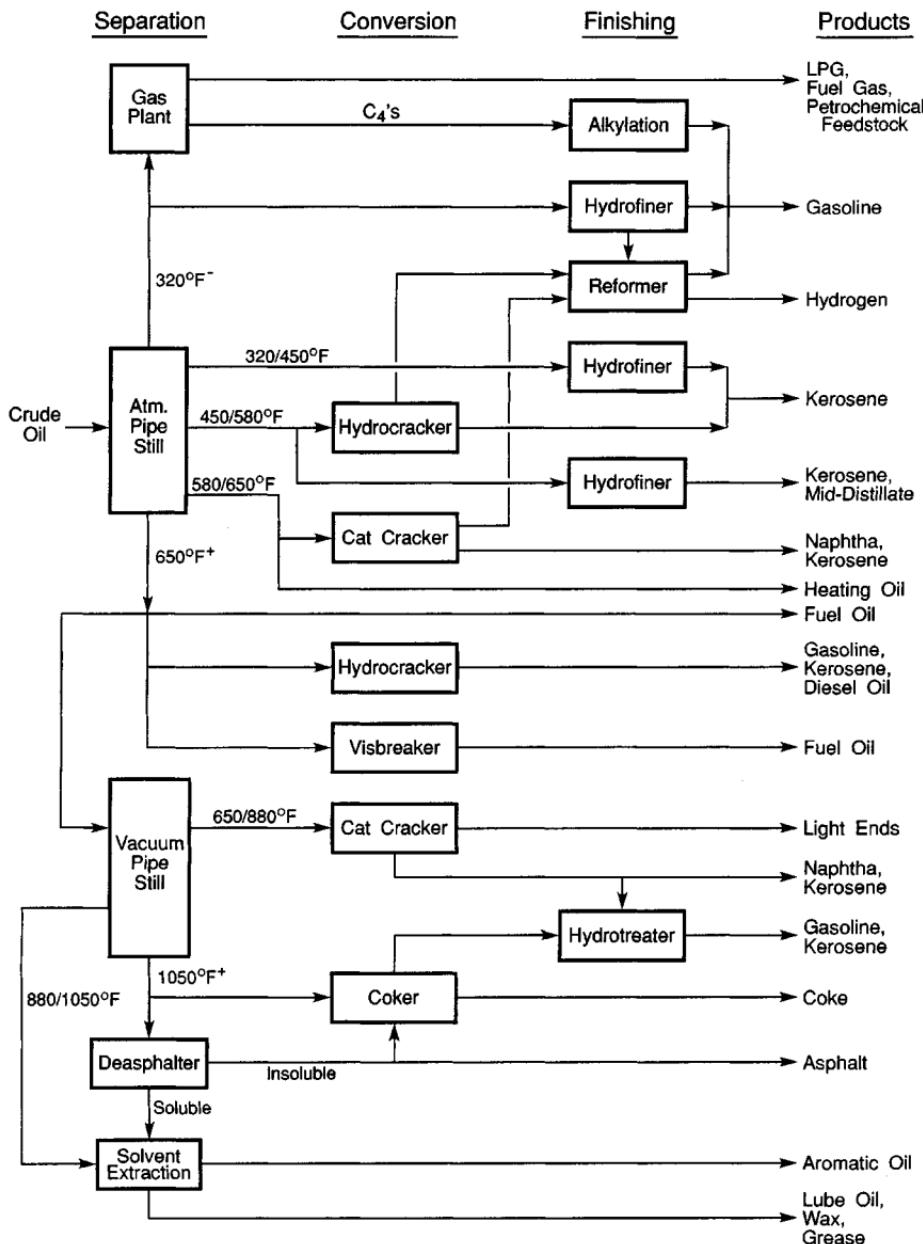


Figure 13.1. Schematic representation of a petroleum refinery (from Speight, 1999).

blended. This chemical reaction results in the formation of a new product that, when soluble, affects the properties of the blend and, when insoluble, settles out in form of semisolid or solid matter.

Instability occurs because of a low resistance of the product to environmental (in use) influences during storage or because of its susceptibility to oxidative and/or other degradative processes. In the 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 solubility of the secondary products and they will appear as sludge or sediment that can be separated by filtration 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 fuel 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 in certain fuels and lubricants (ASTM D-2532). Usually, the viscosity change might be due to separation of paraffins as might occur when diesel fuel and similar engines are allowed to cool and stand unused overnight in low-temperature climates.

It is not only product complexity that affects crude oil use. It is also the nature of the crude oil itself. Many crude oils form degradation products in the form of sludge and deposits that settle at the bottom of storage facilities, reducing the available storage space and causing operational difficulties. The formation of sludge and deposits from crude oil is dependent on the presence of certain components, sometimes contaminants, as well as on handling and storage conditions.

Impurities such as water, sand, dust, or corrosion products are often precursors for sludge, deposits, and sediments found at the bottom of crude oil storage tanks. The presence of wax may aggravate this problem still more. Another cause for degradation product formation in the stored crude oil is the presence of certain constituents in the crude oil, such as naphthenic acids, nitrogen or sulfur compounds, or waxy substances.

The source and the effects of impurities, which may be present in some crude oils, are well known; procedures to eliminate this problem are widely employed. The chemical instability of some crude oils, at certain handling and storage conditions, is another contributor to possible degradation product formation in crude oils during storage. This chemical instability has not been given much attention in the past, probably because of the fact that crude oil, after so many years of existence since its formation, should be stable enough for all practical purposes.

However, it has been observed that some crude oils, when taken out of their natural surroundings and exposed to new environmental conditions, may be affected as to their stability properties under new storage conditions.

As always, it is appropriate to define here some of the terms that are used in the liquid fuels field so that their use later in the text will be clearer and so that some potential for misunderstanding is alleviated. The general scientific areas of instability and incompatibility are complex and have been considered to be nothing better than a black art because not all of the reactions that contribute to instability and incompatibility have been defined (Wallace, 1964; Speight, 1992; Storm et al., 1994; Mushrush and Speight, 1995; Speight, 1999). Nevertheless, recent studies over the past three decades have made valuable contributions to our understanding of instability and incompatibility in fuels. However, for the most part, gaps remain in our knowledge of the chemistry and physics of instability and incompatibility.

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.

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 also 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) (Brinkman and White, 1981). *Thermal oxidative stability* is the ability of the liquid to withstand relatively high temperatures for short periods of time in the presence of oxidation 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 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 fuel as received for testing (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 fuel 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 solid precipitate are measured. A similar test, using an accelerated oxidation procedure, is also in use for determining the oxidative stability of diesel fuel (ASTM D-2274), steam turbine oil (ASTM D-2272), distillate fuel oil (ASTM D-2274), and lubricating grease (ASTM D-942).

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. Existent dry sludge is distinguished from the *potential dry sludge* that is obtained by aging the sample at an elevated temperature.

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.

An analogous test, the *thin film oven test (TFOT)* (ASTM D-1754) and an aging test (IP 390) are used to indicate the rate of change of various physical properties such as penetration (ASTM D-5), viscosity (ASTM D-2170), and ductility (ASTM D-113) after a film of asphalt or bitumen has been heated in an oven for 5 h at 163°C (325°F) on a rotating plate. A similar test is available for the stability of engine oil by thin film oxygen uptake (*TFOUT*) (ASTM D-4742).

This test establishes the effects of heat and air on the basis of changes incurred in the above physical properties measured before and after the oven test. The allowed rate of changes in the relevant bitumen properties after the exposure of the tested sample to the oven test is specified in the relevant specifications (ASTM D-3381).

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

The phenomenon of *instability* is often referred to as *incompatibility* and is more commonly known as *sludge formation*, *sediment formation*, or *deposit formation*. In petroleum and its products, instability often manifests itself in various ways (Stavinoha and Henry, 1981; Hardy and Wechter, 1990a; Ruzicka and Nordensen, 1990; Power and Mathys, 1992; Mushrush and Speight, 1995). Hence, there are different ways of defining each of these terms.

Instability reactions are usually defined in terms of the formation of filterable and nonfilterable sludge (sediments, deposits, and gums), an increased peroxide level, and the formation of color bodies (IP 196). Color bodies in and of themselves do not predict instability; however, the reactions that initiate color body formation can be closely linked to heteroatom-containing (i.e., nitrogen-, oxygen-, and sulfur-containing) functional group chemistry.

Fuel incompatibility can have many meanings. The most obvious example of incompatibility (*nonmiscibility*) is the inability of a hydrocarbon fuel and water to mix. In the present context, incompatibility usually refers to the presence of various polar functions (i.e., heteroatom function groups containing nitrogen, oxygen, or sulfur and even various combinations of the heteroatoms) in the crude oil.

Perhaps the true meaning of the term incompatibility is found when it is applied to refining. The term is applied when a product that is incompatible with (immiscible with or insoluble in) other products is formed in the same reactor. Such an example is the formation of coke during many thermal and catalytic operations. Coke formation is considered to be an initial *phase separation* of an insoluble, solid coke precursor before coke formation proper (Speight, 1999 and references cited therein). In the case of crude oils, *sediments* and *deposits* are closely related to *sludge*, at least as far as compositions are concerned. The major difference appears to be in the character of the material.

There is also the suggestion (often, but not always, real) that the sediments and deposits originate from the inorganic constituents of petroleum. They may be formed from the inherent components of the crude oil (i.e., the metalloporphyrin constituents) or from the ingestion of contaminants by the crude oil during the initial processing operations. For example, crude oils are known to *pick up* iron and other metal contaminants from contact with pipelines and pumps. Sediments can also be formed from organic materials, but the usual inference is that these materials are formed from inorganic materials. The inorganic materials can be salt, sand, rust, and other contaminants that are insoluble in the crude oil and settle to the bottom of the storage vessel.

Gum typically forms by way of a hydroperoxide intermediate that induces polymerization of olefins. The intermediates are usually soluble in the liquid medium. However, gums that have undergone extensive oxidation reactions tend to be higher in molecular weight and much less soluble. In fact, the high-molecular-weight sediments that form in fuels are usually the direct result of *auto-oxidation* reactions. Active oxygen species involved include both molecular oxygen and hydroperoxides. These reactions proceed by a free radical mechanism, and the solids produced tend to have increased incorporation of heteroatom and are thus also more polar and therefore increasingly less soluble in the fuel.

The most significant and undesirable instability change in fuel liquids is the formation of solids, termed *filterable sediment* or, conversely, *filter-blocking bodies* (ASTM D-2068). Filterable sediments can plug nozzles and filters, coat heat exchanger surfaces, and otherwise degrade engine performance. These solids are the result of free radical auto-oxidation reactions. Although slight thermal degradation occurs in nonoxidizing atmospheres, the presence of oxygen or active oxygen species, that is, hydroperoxides, will greatly accelerate oxidative degradation as well as significantly lower the temperature at which undesirable products are formed. Solid deposits that form as the result of short-term high-temperature reactions share many similar chemical characteristics with filterable sediments that form in storage.

Recently, some stability requirements have been defined, and test methods have been introduced for this purpose. Sludge and deposit formation is associated not only with product instability but also with its incompatibility. The main test used currently for this purpose is the *hot filtration test*, which indicates the existent and accelerated dry sludge content of various heavy feedstocks or products. There are additional tests serving the same purpose, such as, for example, the *hot centrifuge test* and the *spot test*.

A compatibility spot test (e.g., ASTM D-4740) is currently used as an estimate of fuel oil compatibility properties. The tendency of a fuel oil, or any heavier feedstock, can be estimated by various thermal stability tests (ASTM D-1661, ASTM D-2070, ASTM D-2160, ASTM D-5483, ASTM D-5579), and even though some of these tests (ASTM D-1661, ASTM D-2160) have been discontinued, they still find use in many laboratories.

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

The chemistry and physics of incompatibility can, to some extent, be elucidated (Wallace, 1969; Hardy and Wechter, 1990b; Power and Mathys, 1992; Mushrush

and Speight, 1995), but many unknowns remain. In addition to the chemical aspects, there are also aspects such as the attractive force differences, e.g.:

- specific interactions between like/unlike molecules (e.g., hydrogen bonding and electron donor-acceptor phenomena) that are also effective;
- field interactions such as dispersion forces and dipole-dipole interactions; and
- any effects imposed on the system by the size and shape of the interacting molecular species.

Such interactions are not always easy to define, and thus the measurement of instability and incompatibility has involved visual observations, solubility in solvents such as trichloroethylene (ASTM D-2042), hot filtration sediment (HFS), and gum formation. However, such methods are often considered to be *after-the-fact methods* because they did not offer much in the way of predictability. In refinery processes (Fig. 13.1) and in terms of product use, predictability is not just a luxury but also a necessity. The same principle must be applied to the measurement of instability and incompatibility. Therefore, methods are continually being sought to aid in achieving this goal.

In addition to the gravimetric methods, there have also been many attempts to use crude oil and/or product characteristics and their relation to the sludge and deposit formation tendencies. In some cases, a modicum of predictability is the outcome, but, in many cases, the data appear as *preferred ranges* and are subject to personal interpretation. Therefore, caution is advised.

It is the purpose of this chapter to document some of the more prominent methods used for determining instability and incompatibility. No preference is shown and none is given to any individual method. Although many of the tests cited in this chapter are cited in other chapters, citations in the context of this chapter are for the sake of completeness and are not to be construed as favoring one test or the other. It remains the choice of the individual analyst and experimentalist to choose the method on the basis of the type of fuel, the immediate needs, and the projected utilization of the data. As elsewhere, it is the careless use of the data that often detracts from an otherwise sound method.

13.2. INSTABILITY AND INCOMPATIBILITY ASSESSMENT

The instability/incompatibility of crude oil and of crude oil products is manifested in the formation of sludge, sediment, and general darkening in color of the liquid (ASTM D-1500, IP 17).

To assess the possibility of gum formation in storage, in other words, the gum stability of the gasoline, a test (ASTM D-525, IP 40) is used that determines, in

a pressure vessel, the *induction period*, or time of heating at 100°C (212°F) with oxygen at an initial pressure of 100 pounds per square inch, that elapses before the oxygen pressure begins to fall because of the oxidation of the sample and the formation of gum therein indicates the onset of oxidative instability (ASTM D-2893, ASTM D-4636, ASTM D-5483, IP 40, IP 48, IP 138, IP 142, IP 157, IP 229, IP 280, IP 306, IP 307, IP 323, IP 328, IP 335, IP 388). The figure for oxidation stability, or *breakdown time* as it is sometimes called, is thus regarded as a measure of the stability of the fuel.

However, because of the multiplicity of types and conditions of storage, it is impossible to equate induction period with safe storage time, but it has been found by long experience that a minimum 240-min induction-period usually ensures a satisfactory level of gum stability for most normal marketing and distributing purposes. Induction period is also a useful control test for determining the amount of gum inhibitor to be added to gasoline, provided that the storage stability of the combination of the gasoline and inhibitor has been established by practical storage experiments.

Sludge (or sediment) formation takes one of the following forms: (1) material dissolved in the liquid, (2) precipitated material, and (3) material emulsified in the liquid. Under favorable conditions, sludge or sediment will dissolve in the crude oil or product, with the potential of increasing the viscosity. Sludge or sediment that is not soluble in the crude oil (ASTM D-96, ASTM D-473, ASTM D-1796, ASTM D-2273, ASTM D-4007, ASTM D-4807, ASTM D-4870) may either settle at the bottom of the storage tanks or remain in the crude oil as an emulsion. In most cases the smaller part of the sludge/sediment will settle satisfactorily and the larger part will stay in the crude oil as emulsions. In any case, there is a need for breaking the emulsion, whether it is a water-in-oil emulsion or the sludge itself, which must be separated into the oily phase and the aqueous phase. The oily phase can be then processed with the crude oil, and the aqueous phase can be drained out of the system.

Phase separation can be accomplished by either the use of suitable surface active agents, allowing for sufficient settling time, or use of a high-voltage electric field for breaking such emulsions after admixing water at a rate of about 5% and at a temperature of about 100°C (212°F).

Emulsion breaking, whether the emulsions are due to crude oil-sludge emulsions, crude oil-water emulsions, or breaking of the sludges themselves into their oily and inorganic components, are of a major importance from operational as well as commercial aspects. With some heavy fuel oil products and heavy crude oils, phase separation difficulties often arise (Ruzicka and Nordenson, 1990; Mushrush and Speight, 1995). Also, some crude oil emulsions may be stabilized by naturally occurring substances in the crude oil. Many of these polar particles accumulate at the oil-water interface, with the polar groups directed toward the water and the hydrocarbon groups toward the oil. A stable interfacial skin may be so formed; particles of clay or similar impurities, as well as wax crystals present in the oil,

may be embedded in this skin and make the emulsion very difficult to break (see Schramm, 1992 and references cited therein).

Chemical and electrical methods for sludge removal and for water removal, often combined with chemical additives, must be used for breaking such emulsions. Each emulsion has its own structure and characteristics, whether water-in-oil emulsions, in which the oil is the major component, or oil in water emulsions, in which the water is the major component. The chemical and physical nature of the components of the emulsion plays a major role in their susceptibility to the various surface active agents used for breaking them.

Therefore, appropriate emulsion-breaking agents must be chosen very carefully, usually with the help of previous laboratory evaluations. Water or oil soluble demulsifiers, the latter being often nonionic surface active alkylene oxide adducts, are used for this purpose. However, as was said in the foregoing, the most suitable demulsifier must be chosen for each case from a large number of such substances in the market by a prior laboratory evaluation.

Some heavy feedstocks (heavy oil and bitumen) have been found to be especially susceptible to sludge formation that is reflected as an increase of viscosity and pour points. In addition, there is a drop in the initial asphaltene content of the treated samples, but during storage this content increases more than that of the untreated samples.

In addition to the stability of the crude oil system, there are many crude oil products that are unstable under service conditions. For example, many products manufactured by cracking processes contain unsaturated components that may oxidize during storage and form undesirable oxidation products. If storage for considerable time before use is anticipated, it is essential that the product should not undergo any deleterious change under storage conditions and should remain stable.

Heteroatoms (particularly nitrogen, sulfur, and trace metals) (Chapter 2) are present in petroleum and might be also expected to be present in liquid fuels and other products from petroleum. Indeed, this is often the case, although there may have been some skeletal changes induced by the refining process(es). Oxygen is much more difficult to define in petroleum and liquid fuels. However, it must be stressed that instability/incompatibility is not directly related to the total nitrogen, oxygen, or sulfur content. The formation of color/sludge/sediment is a result of several factors. Perhaps the main factor is the location and nature of the heteroatom that, in turn, determines reactivity (Mushrush and Speight, 1995).

Compatibility in distillate products is important to commercial interests and consumers as well as to the producer. Distillate products that are made from the refining process based on straight-run distillation show very few incompatibility problems. However at present and in the future, problems for refiners will continue to increase as the quality of the available crude decreases worldwide. This decrease,

coupled with the inevitable future use of liquid fuels from biosources, coal, and shale sources, will exacerbate the present problems for the producers.

When various stocks are blended at the refinery, incompatibility can be explained by the onset of acid-base catalyzed condensation reactions of the various organo-nitrogen compounds in the individual blending stock themselves. These are usually very rapid reactions with practically no observed induction time period (Hardy and Wechter, 1990b).

When the product is transferred to a storage tank or some other holding tank, incompatibility can occur the free-radical hydroperoxide-induced polymerization of active olefins. This is a relatively slow reaction, because the observed increase in hydroperoxide concentration is dependent on the dissolved oxygen content (Mayo and Lan, 1987; Taylor, 1976).

Another incompatibility mechanism involves degradation when the product is stored for prolonged periods, as might occur during stockpiling of fuel for military use (Brinkman et al., 1980; Stavinoha and Westbrook, 1980; Brinkman and Bowden, 1982; Cooney et al., 1985; Goetzinger et al., 1983; Hazlett and Hall, 1985). This incompatibility process involves (1) the buildup of hydroperoxide moieties after the gum reactions, (2) a free-radical reaction with the various organo-sulfur compounds present (such as mercaptan sulfur, R-SH, ASTM D-3227, ASTM D-5305) that can be oxidized to sulfonic acids, and (3) reactions such as condensations between organo-sulfur and nitrogen compounds and esterification reactions.

Incompatibility during refining can occur in a variety of processes, either by intent (such as in the deasphalting process) or inadvertently when the separation is detrimental to the process. Thus separation of solids occurs whenever the solvent characteristics of the liquid phase are no longer adequate to maintain polar and/or high-molecular-weight material in solution.

Examples of such occurrences are:

1. asphaltene separation that occurs when the paraffinic nature of the liquid medium increases (Chapter 9);
2. wax separation that occurs when there is a drop in temperature or the aromaticity of the liquid medium increases (Chapter 5);
3. sludge/sediment formation in a reactor that occurs when the solvent characteristics of the liquid medium change, causing separation (Chapter 9);
4. coke formation that occurs at high temperatures and commences when the solvent power of the liquid phase is not sufficient to maintain the coke precursors in solution (Chapter 9); and
5. sludge/sediment formation in fuel products that occurs because of the interplay of several chemical and physical factors (Mushrush and Speight, 1995).

The reader is referred elsewhere (Speight, 1999, 2000 and references cited therein) for a detailed explanation of the chemical and physical events that occur during refinery operations and result in the formation of a separate phase (Chapter 15).

13.3. DIRECT TEST METHODS

The stability/instability and incompatibility/compatibility of petroleum and its products can be estimated by the use of any one of several test methods that are direct in their approach and are, therefore, considered to be more *objective* in nature. These test methods are:

1. compatibility spot tests (ASTM D-2781, ASTM D-4740);
2. thermal stability test data (ASTM D-873, ASTM D-3241, ASTM D-1660, IP 97);
3. existent and potential sludge formation (hot filtration test); and
4. color (ASTM D-1500).

Most estimates of the susceptibility of feedstocks to compatibility and incompatibility are based on determinations of sludge and suspended solid formation rates when blended with diluents.

13.3.1. Compatibility/Incompatibility Tests

In the compatibility spot test (ASTM D 4740), a drop of the preheated sample is placed in an oven at 100°C (212°F) and after 1 h the spot is examined for evidence of precipitation. At this stage, a stability estimate is obtained. As a second step, a blend consisting of equal amounts of each sample under study is handled similarly and a compatibility estimate is so obtained.

In addition to the test for the stability and compatibility of residual fuels (ASTM D-4740), the other most frequently used stability test is the *existent* and *accelerated dry sludge* content determination of residual fuels and heavy feedstocks (the hot filtration test) (Fig. 13.2). In the hot filtration test (and there are variants of this test), undiluted oil is heated to 100°C (212°F) and filtered at that temperature (usually through a Whatman 50 filter) by applying pressure (72.5 psi, 500 kPa) and pulling a vacuum (2 psi, 13 kPa). The material retained on the filter is washed with heptane, dried, weighed, and reported as a percentage of the sample weight.

Another procedure, sometimes called the *xylene equivalent test*, is based on determination of the proportion of xylene in a blend with *iso*-octane, necessary for obtaining a homogeneous spot on a chromatographic paper when blended with an equal quantity of the specified sample. The lower the proportion of xylene in the diluent, the better is the compatibility of the sample.

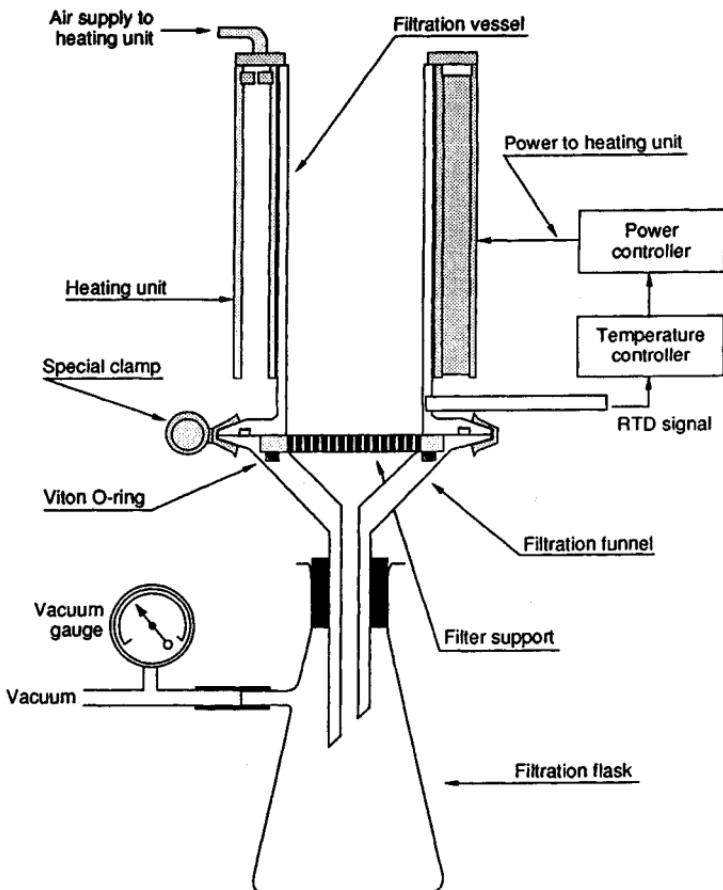


Figure 13.2. Schematic representation of the hot filtration apparatus.

A modified spot test for determining the compatibility of fuel oils or other heavy feedstocks is based on the use of a diluent composed of equal proportions of *n*-heptane and toluene or of two types of gas oils, one a straight-run (paraffinic) gas oil and the second a catalytically cracked (olefinic-aromatic) gas oil. The spots obtained by drops of the sample and diluent blend on a chromatographic paper are evaluated as in the other spot tests, but this modified test is carried out at two temperatures. The results obtained at the higher temperature (usually 63°C, 145°F) indicate asphaltene deposits, whereas at the lower temperature (usually ambient), waxy deposits are indicated.

In the method for the determination of existent dry sludge, the existent dry sludge is determined by the hot filtration method using a filtration temperature in the 100–200°C (212–392°F) range. It was originally developed in the early 1950s to measure the cleanliness of residual fuel oils. The application to process streams,

such as hydrocracking products, involves the measurement of the insoluble components in the sample.

Thus the homogeneous and undiluted sample is passed through a pair of filters at 150°C (300°F). The residual material on the filters is washed with warm heptane (65°C, 150°F), and the filters are dried for 1 h at 110°C (230°F). The incremental weight of the bottom filter as a result of the filtration and solvent wash is taken as an oil adsorption correction and is subtracted from the incremental weight of the top filter. The existent dry sludge is calculated as the nonfilterable material corrected for oil adsorption and expressed as a percentage of the original sample weight.

Hot filtration test results of up to 0.2% w/w are considered to be satisfactory; results above 0.4% w/w indicate a poor stability, but differing values might be required, depending on the intended use of the product.

One test, or property, that is somewhat abstract in its application but is becoming more meaningful is the *solubility parameter* (Chapter 15) (Speight, 1999, 2000). The solubility parameter allows estimations to be made of the ability of liquids to become miscible on the basis of miscibility of model compound types in which the solubility parameter can be measured or calculated.

Although the solubility parameter is often difficult to define when complex mixtures are involved, there has been some progress. For example, petroleum fractions have been assigned a solubility parameter similar to that of the solvent used in the separation. However, there is also the concept (Speight, 1992) that the solubility parameter of petroleum fractions may be defined somewhat differently because they can be estimated from data such as the atomic hydrogen-to-carbon ratios. Whichever method is the best estimate may be immaterial as long as the data are used to the most appropriate benefit and allow some measure of predictability.

Bottle tests constitute the predominant test method, and the test conditions have varied in volume, type of glass or metal, vented and unvented containers, type of bottle closure. Other procedures have involved stirred reactor vessels under air pressure or under oxygen pressure and small volumes of fuel using a coverslip for solid deposition (ASTM D-4625). All of these procedures are gravimetric in nature.

There are several *accelerated fuel stability tests* that can be represented as a time-temperature matrix (CRC, 1979; Goetzinger et al., 1983; Hazlett, 1992). A graphical representation shows that the majority of the stability tests depicted fall close to the solid line, which represents a doubling of test time for each 10°C (18°F) change in temperature. The line extrapolates to approximately one year of storage under ambient conditions. Temperatures at 100°C (212°F) or higher present special chemical problems.

The phenomenon known as *gum stability* is an approximate measure of the tendency to form gum during storage. Thus 50 ml of the sample (usually gasoline) are placed in a glass dish inside a stainless steel bomb that is filled with oxygen at

100 psi (690 kPa). The bomb assembly is placed in a boiling water bath and connected to a sensitive pressure/time recorder. The time interval in minutes between placing the bomb in the water bath and recording a drop of 2 psi (13.8 kPa) from the maximum pressure is recorded as the induction period (oxygen stability).

To determine the propensity for gum formation, 50 ml of sample are evaporated in a glass dish of specified size on a steam bath for 1 h, or until evaporation is complete, while heated air from a small jet impinges on the surface. The dish is transferred to a drying oven for 1 h and weighed after cooling. The weight in mg/100 ml is reported as existent gum (ASTM D-381, IP 131).

It is also worthy of note that *fractionation* of petroleum and its products may also present an indication of stability or instability. There are many schemes by which petroleum and related materials might be fractionated. It is not intended to repeat the details of these schemes in this chapter. However, a brief overview is necessary because fractional composition can play a role in stability and incompatibility phenomena.

13.3.2. Water Content, Salt Content, and Bottom Sediment/Water (BS&W)

Water and salt contents of crude oils produced at the field (ASTM D-96) can be very high, sometimes forming its major part. The salty water is usually separated at the field, usually by settling and draining; surface active agents as electrical emulsion breakers (desalters) are sometimes used. The water and salt contents of crude oil supplied to the buyers is a function of the production field. Water content below 0.5%, salt content up to 20 pounds per 1000 barrels, and bottom sediment and water up to 0.5% are considered to be satisfactory.

The higher the bottom sediment and water content, the higher sludge and deposit formation rates that can be expected in the stored crude oil.

Water content (ASTM D-1096, ASTM D-1401, ASTM D-1744, ASTM D-3240, ASTM D-3948, ASTM D-4006, ASTM D-4007, ASTM D-4377, ASTM D-4860, ASTM D-4928, IP 289, IP 358, IP 412, IP 438, IP 439), salt content (ASTM D-3230, IP 77), and bottom sediment/water (ASTM D-95, ASTM D-96, ASTM D-1796, ASTM D-4007, IP 74, IP 75) indicate the concentrations of aqueous contaminants either present in the crude originally or picked up by the crude during handling and storage. Sediment can also be determined by an extraction method (ASTM D-473) and by a membrane filtration method (ASTM D-4807). In addition, the former method (ASTM D-473) uses an extraction procedure and can be used to differentiate between inorganic sediment and organic sediment, offering an option of determining extraneous components (such as clay, silt, sand rust, catalyst fines, and coke) from the inherent organic constituents of the sample.

Although the centrifuge methods are still used (ASTM D-96, ASTM D-1796, ASTM D-2709 and ASTM D-4007), many laboratories prefer the Dean and Stark

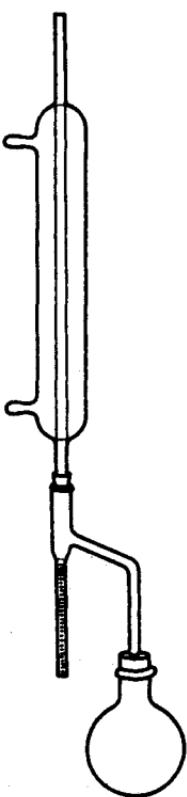


Figure 13.3. Dean and Stark distillation.

method adaptor (ASTM D-95). The apparatus consists of a round-bottom flask of 50-ml capacity connected to a Liebig condenser by a receiving tube of 25-ml capacity, graduated in 0.1 ml (Fig. 13.3). A weighed amount corresponding to approximately 100 ml of oil is placed in the flask with 25 ml of dry toluene. The flask is heated gently until the 25 ml of toluene have distilled into the graduated tube. The water distilled with the toluene separates to the bottom of the tube, where the volume is recorded in milliliters, the weight in milligrams or as a percentage.

To determine the sediment in petroleum or in a petroleum product, the method involves solvent extraction (Fig. 13.4). Inside a 1-liter Erlenmeyer flask is suspended a cold finger condenser, which drops into a porous alumina thimble of dimensions 2.75 in. \times 0.6 in. (70 \times 15 mm). The thimble is cleaned with benzene and dried before the test and 10 g of sample are introduced. Approximately 100 ml of benzene are placed in the flask, which is heated until the condensed benzene vapor, dripping from the cold finger through the thimble, has extracted all the

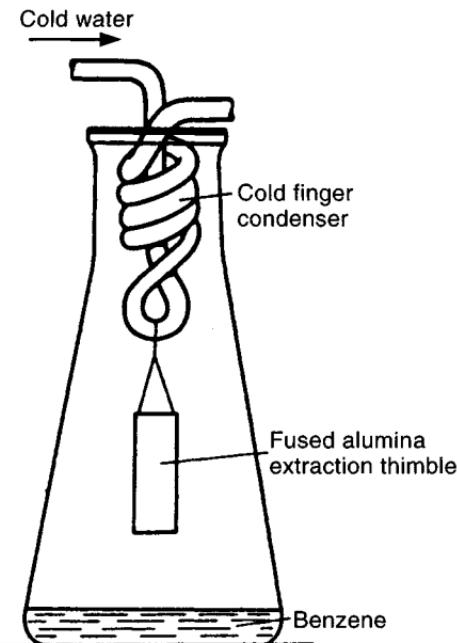


Figure 13.4. Determination of sediment by extraction.

sample. The thimble is then dried and reweighed, and the increase in weight is recorded as a percentage or as mg sediment/100 ml sample.

The Karl Fischer reagent method (ASTM D-1744), the Karl Fischer titration method (ASTM D-377), and the colorimetric Karl Fischer titration method (ASTM D-4298) still find wide application in many laboratories for the determination of water in liquid fuels, specifically the water content of aviation fuels.

13.3.3. Fractionation

Petroleum can be fractionated by a variety of methods (Speight, 1999), but the most common method involves fractionation into four broad fractions (Fig. 13.5) (Chapter 9), starting with precipitation of the asphaltene fraction and the use of adsorbents to fractionate the deasphalting oil. Thus studies of the composition of the incompatible materials often involve determination of the distribution of the organic components by *selective fractionation* that is analogous to the deasphalting procedure and subsequent fraction of the deasphaltened oil (maltenes):

1. deasphaltened oil or deasphalting oil, i.e., heptane soluble materials: often called maltenes or petrolenes;

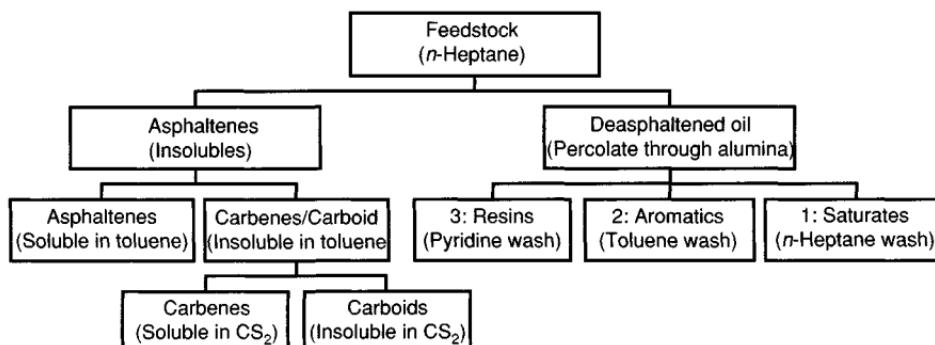


Figure 13.5. Feedstock fractionation.

2. heptane-insoluble material, benzene (or toluene)-soluble material, often referred to as asphaltenes;
3. benzene (or toluene)-insoluble material: referred to as carbenes and carboids when the fraction is a thermal product; and
4. pyridine-soluble material (carbenes) and pyridine-insoluble material (carboids).

Carbon disulfide and tetrahydrofuran (c.f. page 350) have been used in place of pyridine. The former, although having an obnoxious odor and therefore not much different from pyridine, is easier to remove because of the higher volatility.

In addition to toluene (ASTM D-4312), quinoline is also used to determine the insoluble materials in tar and pitch (ASTM D-2415, ASTM D-4746), but removal of the high-boiling solvent to retrieve the sample is difficult. Dimethylformamide has also been used to separate insoluble material from tar and pitch (ASTM D-2764). Presumably the dimethylformamide removes a *saturates fraction* as insoluble material (Speight, 1999, p. 267) but, again, removal of the solvent from the product fractions is difficult if further (accurate) analysis is required.

Tetrahydrofuran is not as well established in petroleum science as it is in coal liquid-related research. Thus it is more than likely that the petroleum researcher will use carbon disulfide or pyridine, or some suitable alternate solvent. It may also be necessary to substitute cyclohexane as an additional step for treatment of the heptane-insoluble materials before treatment with benzene (or toluene). The use of quinoline has been suggested in place of pyridine, but this solvent presents issues associated with the high boiling point of the solvent.

Fractionation procedures allow a before-and-after inspection of any feedstock or product and can give an indication of the means by which refining or use changes the composition of the feedstock. In addition, fractionation also allows studies to

be made of the interrelations between the various fractions. For example, the most interesting phenomenon (in the present context) to evolve from the fractionation studies is the relationship between the asphaltenes and the resins.

13.4. INDIRECT TEST METHODS

A number of experimental methods are available for inspection of the feedstock and products that (on a before and after basis) can assist in the estimation of the events that reflect and most probably influence the instability and incompatibility of petroleum and its products. These factors have been explored and attempts made to estimate the character of the fuel or product with varied results.

The series of tests in this section are considered to be *indirect* in their approach to the determination of instability and incompatibility and are, therefore, considered to be *subjective* in nature.

13.4.1. Elemental Analysis and Metals (Ash) Content

The ultimate analysis (elemental composition) of petroleum and its products is not reported to the same extent as for coal (Berkowitz, 1979; Hessley et al., 1986; Speight, 1994a). Nevertheless, there are ASTM procedures for the ultimate analysis of petroleum, heavy oil, bitumen, and their respective products (Chapter 4):

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);
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, ASTMD-3177, ASTMD-4045 and ASTMD-4294, ASTM E-443, IP 30, IP 61, IP 103, IP 104, IP 107, IP 154, IP 243); and
5. *metals and ash content* (ASTM D-482, ASTM D-1026, ASTM D-1262, ASTM D-1318, ASTM D-1368, ASTM D-1548, ASTM D-1549, ASTM D-2547, ASTM D-2599, ASTM D-2788, ASTM D-3340, ASTM D-3341, ASTM D-3605, ASTM D-4422, IP 223).

but many such methods may have been designed for other materials.

In terms of the instability and incompatibility of petroleum and petroleum products, the heteroatom content appears 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 fuels of specified 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.

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), 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 in. \times 0.5 in. (75 \times 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.
Back, 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).

The majority of crude oils contain metallic constituents (Speight, 1999, 2000) that are often determined as combustion ash (ASTM D-482). Many of the metals occur in sediments and are analyzed after digestion of the sediment (ASTM D-4698). This is particularly so for the heavier feedstocks. These constituents, of which nickel and vanadium are the principal metals, are very influential in regard to feedstock behavior in processing operations.

The metal (inorganic) constituents of petroleum or a liquid fuel arise from either those present in the crude oil originally or those picked up by the crude oil during

storage and handling. The former are mostly metallic substances like vanadium, nickel, sodium, iron, silica, etc.; the latter may be contaminants such as sand, dust, and corrosion products.

Ash (Chapter 4) is the percentage by weight of inorganic residue obtained by the combustion of petroleum or a petroleum product in a porcelain, silica, or platinum dish. The temperature of combustion is not specified, but the final temperature reached is preferably 800°C (1470°F).

Thus a weight amount (approximately 20 g) of sample is placed in a clean, dry, weighed silica dish. This is placed inside a cold electric muffle furnace. The temperature is raised slowly until the oil burns when a flame is applied to the surface. When combustion is complete, the temperature of the muffle is raised to 800°C (1470°F) and maintained at this temperature for another hour. The crucible and ash are then cooled and reweighed, and the weight of ash is obtained by difference.

Incompatibility, leading to deposition of the metals (in any form) on the catalyst leads to catalyst deactivation whether it be by physical blockage of the pores or destruction of reactive sites. In the present context, the metals must first be removed if erroneously high carbon residue data are to be avoided. Alternatively, they can be estimated as ash by complete burning of the coke after carbon residue determination.

Metals content above 200 ppm are considered to be significant, but the variations are very large. The higher the ash content, the higher is the tendency of the crude oil to form sludge or sediment.

13.4.2. Density/Specific Gravity, Viscosity, and Pour Point

In the earlier years of the petroleum industry, *density* and *specific gravity* (with the *API gravity*) (Chapter 4) were the principal specifications for feedstocks and refinery products (Speight, 1999, 2000 and references cited therein). They were used to give an estimate of the most desirable product, that is, kerosene, in crude oil. At the present time, a series of standard tests exists for determining density and specific gravity (Chapter 4).

There is the suggestion of a relationship between the density or specific gravity of crude oils and their sludge-forming tendencies because crude oils having a higher density (thus a lower API gravity) are generally more susceptible to sludge formation, presumably because of the higher content of the polar/asphaltic constituents.

Viscosity is a measure of fluidity properties and consistencies at given temperatures (Chapter 4), and it varies with the origin and type of the feedstock and also with the nature of chemical constituents, particularly the polar functions, in which intermolecular interactions can occur (Speight, 1999, 2000). Heavier crude oils, i.e., crude oils of lower API gravity, have usually higher viscosity. Increases of

viscosity during storage indicate either an evaporation of volatile components or formation of degradation products dissolving in the crude oil.

Products of the instability or incompatibility processes usually increase the viscosity of the petroleum product. Standing at low temperatures will also cause a viscosity change in certain fuels (ASTM D-2532). The viscosity change might be caused by separation of paraffins as might occur when diesel fuel and similar engines are allowed to cool and stand unused overnight in low-temperature climates.

The *pour point* (Chapter 5) defines the cold properties of crude oils and petroleum products, i.e., the minimal temperature at which they still retain their fluidity (ASTM D-97). In addition to the pour point (ASTM D 97), the *cloud point* (ASTM D 2500) and the *cold filter plugging point* (IP 309) are also used to determine the compatibility of crude oils and crude oil products. The first two tests, like viscosity, are estimates of sample *fluidity*; the third test is an estimate of the *filterability* of a sample (e.g., ASTM D-4539, IP 309, IP 387, IP 419, IP 448).

The properties of many liquid fuels are directly influenced by the concentration, size, and form of wax crystals that are formed when the fuel is cooled. Higher concentrations of large-sized wax crystals are detrimental to the free flow of the fuel, i.e., they increase its pour point. Wax crystals of a needlelike form, even when not too large, interfere with the filterability of the fuel.

Higher-pour point crude oils are sometimes more waxy, and therefore they tend to form waxlike materials that enhance sludge formation. On the other hand, heavy oil and bitumen often exhibit high pour point, and the susceptibility of these feedstocks to oxidation often results in instability and incompatibility that is reflected in the formation of a separate phase (sludge or sediment).

13.4.3. Volatility

Petroleum can be subdivided by distillation into a variety of fractions of different *cut points* (Fig. 13.6; Chapter 5). In fact, distillation was, and still is, the method by which feedstocks are evaluated as being suitable for various refinery options. Indeed, volatility is one of the major tests for petroleum products, and it is inevitable that the majority of products will, at some stage of their history, be tested for volatility characteristics (Chapter 5).

As an early part of characterization studies, a correlation was observed between the quality (such as the carbon residue) of petroleum fractions and their hydrogen content (Fig. 13.7) because gasoline, kerosene, diesel fuel, 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.

The very nature of the distillation process by which residua are produced (Speight, 1999, 2000), i.e., removal of distillate without thermal decomposition,

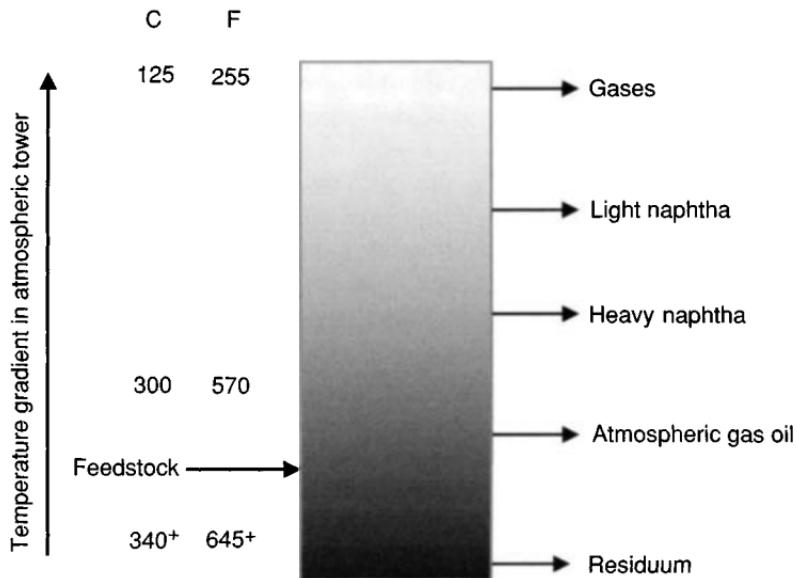


Figure 13.6. Distillation of petroleum into various fractions.

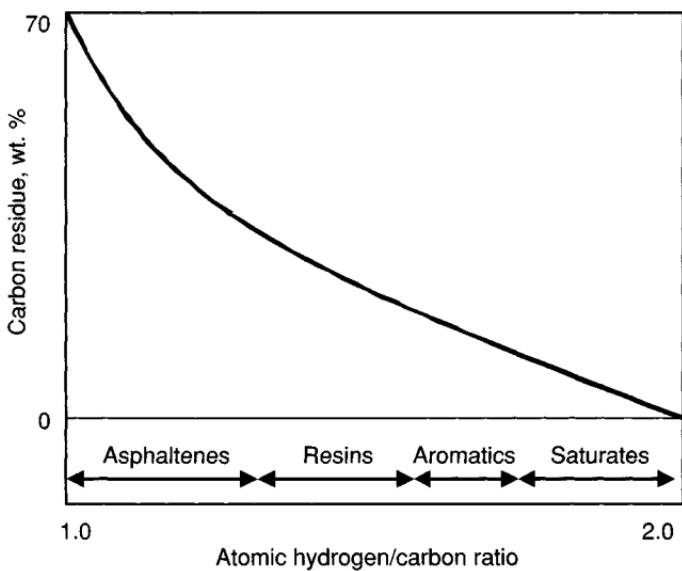


Figure 13.7. Correlation of carbon residue with hydrogen content.

dictates that the majority of the heteroatoms, which are predominantly in the higher-molecular-weight fractions, will be concentrated in the higher-boiling products and the residuum (Speight, 2000). Thus the inherent nature of the crude oil and the means by which it is refined can seriously influence the stability and incompatibility of the products.

In general terms, heavier crude oils, yielding higher amounts of residua, tend to form more sludge during storage compared with light crude oils.

In terms of product use, engine oil that has seen service might contain volatile constituents that can be removed by stripping (ASTM D-3607) or detected by gas chromatography (ASTM D-5480) (Chapter 10). The used oil might also contain solid material (IP 316).

13.4.4. Asphaltene Content

Asphaltenes are dark brown to black friable solids that have no definite melting point and usually intumesce on heating with decomposition to leave a carbonaceous residue. They are obtained from petroleum by the addition of a nonpolar solvent (such as a liquid hydrocarbon) (Fig. 13.5; Chapter 9). Liquids used for this purpose are low-boiling petroleum naphtha, petroleum ether, *n*-pentane, *iso*-pentane, *n*-heptane, and the like (Table 13.1; Girdler, 1965; Mitchell and Speight, 1973; Speight et al., 1982, 1984; Andersen and Birdi, 1990; Speight, 1994b). Usually, the asphaltenes are removed by filtration through paper, but more recently a membrane method has come into use (ASTM D-4055). Liquid propane is used commercially in processing petroleum residues for asphaltenes and resins (Speight, 1999, 2000). Asphaltenes are soluble in liquids such as benzene, toluene pyridine, carbon disulfide, and carbon tetrachloride.

The asphaltene fraction of feedstocks (Fig. 13.5) is particularly important because as the proportion of this fraction increases, there is a concomitant increase

Table 13.1. Standard Method for Asphaltene Precipitation

Method	Precipitant	Volume Precipitant Per g of Sample
ASTM D-893	<i>n</i> -pentane	10 ml
ASTM D-2006	<i>n</i> -pentane	50 ml
ASTM D-2007	<i>n</i> -pentane	10 ml
ASTM D-3279	<i>n</i> -pentane	100 ml
ASTM D-4124	<i>n</i> -pentane	100 ml
IP 143	<i>n</i> -pentane	30 ml
Syn crude method	<i>n</i> -pentane	20 ml

in thermal coke carbon residue and an increase in hydrogen demand as well as catalyst deactivation. The constituents of the asphaltenes form coke quite readily, which is of particular interest in terms of the compatibility/incompatibility of the coke precursors (Speight, 1994b, 1999, 2000).

The effect of asphaltenes and the micelle structure on the state of dispersion also merit some attention. The degree of dispersion of asphaltenes is higher in the more naphthenic/aromatic crude oils because of the higher solvency of naphthenes and aromatics over paraffinic constituents. This phenomenon also acts in favor of the dissolution of any sludge that may form, thereby tending to decrease sludge deposition. However, an increase in crude oil often accompanies sludge dissolution.

The higher the asphaltene content, the greater the tendency of the crude oil to form sludge, especially when blended with other noncompatible stocks.

13.4.5. Acidity

Acidity is a valuable method for measuring or assessing the incompatibility (potential or real) of petroleum and petroleum products (Chapter 8).

The *total acidity* (usually referred to as the *acid number*) is the quantity of base, expressed in milligrams of potassium hydroxide, required to neutralize the acidic constituents in one gram of sample under the conditions of the test (ASTM D-664, ASTM D-974, ASTM D-1093, ASTM D-3242, ASTM D-6441, IP 37, IP 213, IP 431). In actual numbers, it is the number of milliequivalents per gram of alkali required to neutralize the acidity of the petroleum sample.

One method (ASTM D-664) involves dissolution of the sample in a toluene-water-*iso*-propanol (50.0/0.5/49.5) solution titrated potentiometrically with 0.1 N alcoholic potassium hydroxide ($\text{CH}_3\text{CH}_2\text{OH}/\text{KOH}$) using a glass indicating electrode and a calomel reference electrode. The end point is determined either graphically, or if no inflections in the curve are apparent, by titration to a meter reading for a standard buffer solution.

Another standard method (IP 213) involves the determination of the neutralization value of the sample using a potassium hydroxide solution (0.1 N in distilled water) standardized by potentiometric titration with potassium hydrogen phthalate. The sample to be titrated may be dissolved in a toluene-ethanol-water solution. Excess base is added and the mixture is back-titrated with 0.1 N standardized hydrochloric acid to an alkali blue end point.

A modification of this method (ASTM D-6441) uses the solvent systems and reagents as specified (IP 213) but with a direct potentiometric titration using 0.1 N aqueous potassium. A titroprocessor in combination with a lithium chloride (LiCl) combination electrode gives the sensitivity required to identify the end point by inflection.

Two other methods (ASTM D-974 and ASTM D-3339, IP 139) also involve colorimetric titration to determine the acid number of petroleum products and

lubricants by titration with 0.1 N potassium hydroxide in a toluene-isopropyl alcohol mixture to a *p*-naphtholbenzein indicator end point. The application for titration of heavy oil and bitumen is hampered because of the difficulty in detecting the color change from orange to green-brown.

In addition, application of any of the methods to heavy oil and bitumen (or even to whole crude oil) can be influenced by precipitation of asphaltenes on the electrodes during a potentiometric titration. This effect can delay the response of the electrode. When the precipitation problem is severe, inflections in the titration curve cannot be identified and titration to a buffer end point becomes slow and imprecise.

Indeed, determination of the acid number of heavy oil and bitumen is subject to uncertainties due to the problem of precipitation of components during titration. Reduction of test sample size, use of alternate solvent systems, and minimizing titration time, possibly by using a more concentrated titrant, may improve precision. These factors should be examined to establish a method suitable for these heavy feedstocks.

The *acid number* or *base number* or *neutralization value* either by potentiometric titration (ASTM D-664, ASTM D-2896, ASTM D-4739, IP 176, IP 276, IP 417) or by color-indicator titration (ASTM D-974, IP 139) provides information about the functionality in the sample. Further functionality can be determined by use of *saponification numbers* with the color-indicator titration method (ASTM D-94), the potentiometric titration method (ASTM D-939, IP 2), or the alkalinity of the sample (IP 37).

Acidity that is due to the presence of inorganic constituents (IP-182) is usually not expected in crude oils and products, but organic acidity is found. Acidic character is composed of contributions from strong organic acids and other organic acids. Values above 0.15 mg potassium hydroxide per gram are considered to be significantly high. Crude oils of higher acidities may exhibit a tendency of instability.

The acid-imparting agents in crude oils are naphthenic acids and hydrogen sulfide. These are sometimes present in the crude oil originally in small and varying concentrations. They are also present in sludge or sediment formed from petroleum and petroleum products (ASTM D-4978) and can impart acidity to the petroleum or petroleum product (ASTM D-4569). Normally, the total acidity of crude oils is in the range of 0.1–0.5 mg potassium hydroxide per gram, although higher values are not exceptional.

Free hydrogen sulfide is often present in crude oils, with a concentration of up to 10 ppm being acceptable in spite of its toxic nature. However, higher hydrogen sulfide concentrations are sometimes present, with 20 ppm posing serious safety hazards. Additional amounts of hydrogen sulfide can form during the crude oil processing when hydrogen reacts with some organic sulfur compounds, converting them to hydrogen sulfide. In this case, it is referred to as potential hydrogen sulfide,

contrary to free hydrogen sulfide. There are, however, serious consequences to the presence of hydrogen sulfide (real or perceived) in petroleum products, and tests are necessary to ensure its absence (e.g., ASTM D-5705, ASTM D-6021, IP 103, IP 399, IP 401).

Acidity can also form by bacterial action, because some species of aerobic bacteria can produce organic acids from organic nutrients. On the other hand, anaerobic sulfate-reducing bacteria can generate hydrogen sulfide, which, in turn, can be converted to sulfuric acid (by bacterial action).

One method (ASTM D-664) involves dissolution of the sample in a toluene-water-*iso*-propanol (50.0/0.5/49.5) solution titrated potentiometrically with 0.1 N alcoholic potassium ($\text{CH}_3\text{CH}_2\text{OH}/\text{KOH}$) using a glass indicating electrode and a calomel reference electrode. The end point is determined either graphically, or if no inflections in the curve are apparent, by titration to a meter reading for a standard buffer solution.

Another standard method (IP 213) involves the determination of the neutralization value of asphalt (bitumen) using a potassium hydroxide solution (0.1 N in distilled water) standardized by potentiometric titration with potassium hydrogen phthalate. The sample to be titrated may be dissolved in a toluene-ethanol-water solution. Excess base is added and the mixture is back-titrated with 0.1 N standardized hydrochloric acid to an alkali blue end point.

A modification of this method (ASTM D-6441) uses the solvent systems and reagents as specified (IP 213) but with a direct potentiometric titration using 0.1 N aqueous potassium. A titroprocessor in combination with a lithium chloride (LiCl) combination electrode gives the sensitivity required to identify the end point by inflection.

Two other methods (ASTM D-974 and ASTM D-3339) also involve colorimetric titration to determine the acid number of petroleum products and lubricants by titration with 0.1 N potassium hydroxide in a toluene-isopropyl alcohol mixture to a *p*-naphtholbenzein indicator end point. The application for titration of heavy oil and bitumen is hampered because of the difficulty in detecting the color change from orange to green-brown.

In addition, application of any of the methods to heavy oil and bitumen (or even to whole crude oil) can be influenced by precipitation of asphaltenes on the electrodes during a potentiometric titration. This effect can delay the response of the electrode. When the precipitation problem is severe, inflections in the titration curve cannot be identified and titration to a buffer end point becomes slow and imprecise.

13.4.6. Characterization Factors

A series of characterization indices (Chapter 3) can also be used in attempts to determine whether a petroleum product is stable or unstable. For example, the

characterization factor indicates the chemical character of the crude oil and has been used to indicate whether a crude oil was paraffinic in nature or a naphthenic/aromatic crude oil.

The *characterization factor* (sometimes referred to as the *Watson characterization factor*) (Chapter 3) is a relationship between boiling point and specific gravity:

$$K = T_b^{1/3}/d$$

where T_b is the cubic average boiling point, degrees Rankine ($^{\circ}\text{F} + 460$) and d is the specific gravity at 15.6°C (60°F).

The characterization factor was originally devised to illustrate the characteristics of various feedstocks. Highly paraffinic oils have $K = 12.5\text{--}13.0$, whereas naphthenic oils have $K = 10.5\text{--}12.5$. In addition, if the characterization factor is above 12, the liquid fuel or product might, because of its paraffinic nature, be expected to form waxy deposits during storage.

The *viscosity-gravity constant* (vgc) (ASTM D-2501) was one of the early indices proposed to classify petroleum on the basis of composition. It is particularly valuable for indicating a predominantly paraffinic or naphthenic composition.

The constant is based on the differences between the density and specific gravity for the various hydrocarbon species:

$$\text{vgc} = [10d - 1.0752 \log(\nu - 380)]/[10 - \log(\nu - 38)]$$

where d is the specific gravity and ν is the Saybolt viscosity at 38°C (100°F). For viscous crude oils (and viscous products) where the viscosity is difficult to measure at low temperature, the viscosity at 99°C (210°F) can be used:

$$\text{vgc} = [d - 0.24 - 0.022 \log(\nu - 35.5)]/0.755$$

In both cases, the lower the index number, the more paraffinic the sample. For example, a paraffinic sample may have a vgc on the order of 0.840 whereas the corresponding naphthenic sample may have an index on the order of 0.876.

The obvious disadvantage is the closeness of the indices, almost analogous to comparing crude oil character by specific gravity only where most crude oils fall into the range $d = 0.800\text{--}1.000$. The API gravity expanded this scale from 5–60, thereby adding more meaning to the use of specific gravity data.

In a similar manner, the *correlation index*, which is based on a plot of the specific gravity (d) versus the reciprocal of the boiling point (K) in K ($K = \text{degrees Kelvin} = ^{\circ}\text{C} + 273$) for pure hydrocarbons, adds another dimension to the numbers:

$$\text{Correlation Index (CI)} = 473.7d - 456.8 + 48640/K$$

In the case of a petroleum fraction, K is the average boiling point determined by the standard distillation method.

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 benzene is given a value of CI = 100 (Chapter 3). Values between 0 and 15 indicate a predominance of paraffinic hydrocarbons in the sample and values from 15 to 20 indicate predominance either of naphthenes or of mixtures of paraffins/naphthenes/aromatics; a CI value above 50 indicates a predominance of aromatics in the fraction.

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CHAPTER

14

USE OF THE DATA—THE STRUCTURE OF PETROLEUM

14.1. INTRODUCTION

When the data from the various analytical test and investigations have been collected (Chapters 4 to 12), the obvious question that comes to mind relates to use of the data. For the most part, the data are used to determine whether or not a crude oil may produce a certain product and whether or not the product meets specifications. However, since the early days of analysis, there has been a growing tendency to use the analytical data as a means of more detailed and accurate projections with a higher degree of predictability. And at no time has this been more important than when heavy crude oil and bitumen entered the refinery scene.

This direction had been coming over the past four decades, and now the focus divides itself into two approaches: (1) developing a theory of the structure of petroleum and (2) using analytical data to construct maps of petroleum that can be used for predictability of behavior during recovery and refinery operations. A third category, namely, the ability of a product to meet specifications, will remain much the same, but it is the first two categories that help determine the methods by which the product should be produced from the feedstock.

The structure of petroleum has been a topic of some interest for at least five decades since the first theory of petroleum structure was published (Pfeiffer and Saal, 1940). Indeed, studies of petroleum structure present indications of the interactions and interrelationships of the constituents, and the implications of petroleum structure relate to recovery operations as well to refinery operations.

However, to discuss the chemical and physical structure of petroleum, it is necessary to give consideration to the chemical and physical nature of the constituents of petroleum. The chemical nature of the various constituents of petroleum has been addressed elsewhere (Chapter 2) (Speight, 1999, 2000) with some reference to the physical nature of petroleum, and it is not intended to repeat these discourses here. It is however, necessary to understand the interrelationships of the various constituents. Furthermore, it is essential that it be understood not only that petroleum is a *continuum* among the lower-molecular-weight ranges but also that the continuum is complete and continues into the higher-molecular-weight ranges.

The basic concept is that petroleum is a continuum of structural types that may be further defined in terms of polarity and molecular weight (or boiling point) and

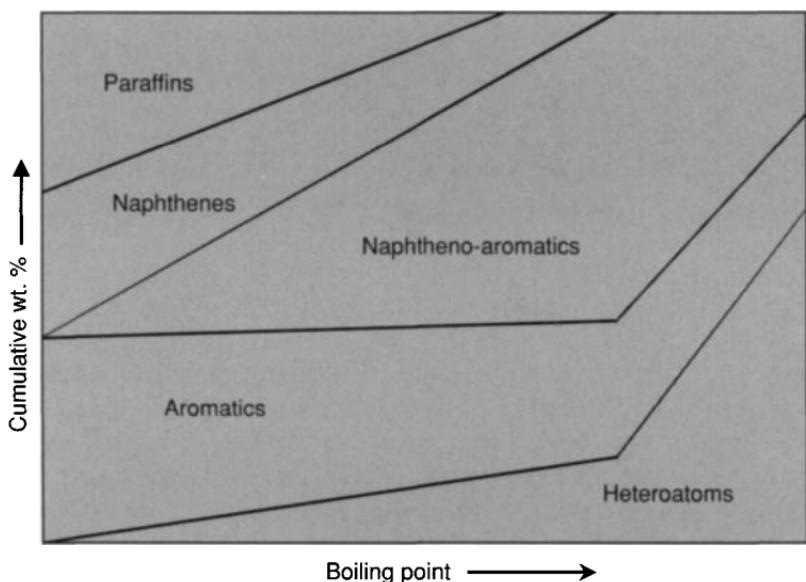


Figure 14.1. Representation of the composition of petroleum.

has been generally accepted for several decades (Long, 1979, 1981; Speight, 1994, 1999, 2000 and references cited therein). These types are isolated and characterized by a variety of techniques (Chapters 8, 9, 10, and 11). The initial focus in this concept was on the hydrocarbon types that occurred in the volatile fractions (Fig. 14.1) (Chapter 5), leaving the characterization of the nonvolatile fractions open to the use of other methods such as spectroscopic techniques and structural group analysis (Chapter 11). Further work on nonvolatile gas oils has shown that the continuum is ubiquitous, or at least sufficient to include such fractions.

Within the distillates, the physical and chemical properties are known to change only gradually with the boiling point, allowing data extrapolation with reasonable certainty. Whenever the range of distillates is expanded, first by vacuum distillation and then by short-path distillation (Chapter 5), the new distillate portions of the previously *nondistillable* residua follow the same patterns as the previous distillates, and relationships between the various physical properties such as structural types (Chapters 2 and 11), molecular weight (Chapter 12), sulfur content, and nitrogen content (Chapter 4) can be extended into the higher-molecular-weight regions.

Thus there is no reason to refute or deny the existence of the continuum from the lower-molecular-weight species to the highest-molecular-weight highest polarity species. Indeed, there is sufficient evidence to extol and embrace the concept of a complete continuum of structural types throughout the whole range of petroleum constituents, be they hydrocarbon or heteroatom in nature (Speight, 1999, 2000).

It is the purpose of these final two chapters to address the issues of petroleum structure and predictability as they affect recovery and refinery operations. In this chapter the focus is on developing a theory of the structure of petroleum, and in the next chapter (Chapter 15) the focus is on using analytical data to construct maps of petroleum that can be used for predictability of behavior during refinery operations. Cross-references are made in both chapters to the relevant chapters in other parts of this book in which the tests are described.

Also included in this chapter is reference to the stability of the petroleum system and recognition of those perturbations that influence this stability. The issues relating to the composition and structural types that occur in the gas oil and resin fractions are not addressed here because considerable detail has been given about the constituents of the various fraction in various sources (Gruse and Stevens, 1960; Altgelt and Boduszynski, 1994; Speight, 1999, 2000 and references cited therein). Thus it would be inappropriate to reproduce all of the relevant work here. This chapter is concerned with how the various constituents interact and coexist, and there is only brief and necessary reference to the various chemical types in the fractions.

14.2. THE STRUCTURE OF PETROLEUM

The chemical (Chapter 8) and physical (Chapters 4 and 5) properties of petroleum are the sum total of the composition (Chapter 2) and interactions of its individual molecules; the system essentially obeys the adage that *the whole is greater than the sum of the individual components*.

The constituents of petroleum (Chapter 2) interact with one another through a variety of secondary bonds or association forces that are generally one to two orders of magnitude weaker than the covalent chemical bonding forces that hold the atoms together in the molecule. The association forces (Chapter 12) are significantly different from covalent bonding forces in that they form bonds that are generally reversible and are usually in dynamic equilibrium. That is, they *form* and *break* under forces induced by such factors as temperature and external stress, and thus they largely determine the physical properties of the composite material.

For example, the nonpolar hydrocarbon components such as those that are dominant in the saturate fraction (Chapter 9) exhibit only weak interaction forces, which accounts for the nonassociative low molecular weight (Chapter 12) and the rather fluid character of this fraction. On the other hand, the asphaltene constituents (Chapter 9) containing condensed aromatic and naphthenic ring systems as well as chemical functional groups containing nitrogen, oxygen, and sulfur atoms may be highly polar or polarizable and thus interact strongly with each other to produce the observed associative high molecular weight (Chapter 12) (Speight, 1994, 1999). Although other factors also play a role, chemical

functionality (Chapter 8) becomes a major consideration in understanding petroleum structure and properties. In summary, and irrespective of the differences in chemical structure and functionality of the constituents, the constituents of petroleum are compatible (Chapter 13).

Compatibility in petroleum deals with the mutual miscibility and existent solubility of a variety of components with widely differing solubility and solvent power (Chapter 13). In terms of the asphaltene constituents (Chapter 9), compatibility has been described using terms such as peptization and dispersability (of asphaltenes in the maltenes) and has been found to be feedstock dependent (Koots and Speight, 1975). This leads to the concept of *molecular structuring* that is analogous to the *lock and key mechanism* so often used to describe *donor-acceptor interactions* in the field of molecular biology. In short, it appears that the resin constituents (Chapter 9) and the asphaltene constituents (Chapter 9) have structural and electronic configurations that are complementary to each other in any one specific crude oil, heavy oil, or bitumen. Whether these relationships can exist between resin and asphaltene constituents from different feedstock families is very questionable, there being evidence to indicate that such a relationship is unlikely (Koots and Speight, 1975).

Thus the relationships of petroleum constituents (Chapter 2) to one another are an essential factor in determining the structure of petroleum, heavy oil, and bitumen systems. There is a multitude of structural types in petroleum, and much effort has been given to the identification of these constituents (Chapters 2 and 11). However, it is not only the structures of the constituents that determine the structure of petroleum but also the means by which these constituents relate to one another.

For example, the reactivity of molecular species can be assessed on the basis of bond energies, but the reactivity of a particular bond is also subject to its environment. In the present context, the relationships of petroleum constituents to one another are also subject to the environment, and a major determinant of this relationship is stereochemistry of the constituents as they relate to one another. It must be appreciated that the stereochemistry of organic compounds is often a major factor in determining reactivity and properties (Eliel and Wilen, 1994).

The available evidence indicates that the hydrocarbon structures, the heteroatom systems, and some features such as the various condensed ring systems in different crude oils are similar (from the asphaltenes and resins to the constituents of the aromatics fraction and saturates fractions) but not the same. A wide variety of source materials are involved in petroleum genesis (Speight, 1999). Thus, on a molecular scale, there are substantial structural differences in the relative proportions of the constituents of different crude oils as dictated by regional variations in the composition of the first-formed *protopetroleum* and the maturation conditions.

The structural differences in different crude oils are reflected in the difficulty with which resins from one crude oil peptize asphaltenes from a different crude oil and the instability (Chapter 13) of the *blend* (Koots and Speight, 1975). For reference, in asphaltene science as in colloid science, the terms *peptized*, *dispersed*, and *solubilized* are often used interchangeably to describe the means by which asphaltenes exist within petroleum.

The assignment of specific molecular configurations to the asphaltene constituents may be of limited value to petroleum technology and certainly beyond the scope of the available methods (Chapter 11) to derive such formulae. However, a variety of structures exist in the asphaltene fraction (in which there is a decided hydrogen deficiency) as dictated by various separation and identification methods (Chapters 9 and 11). But the close relationships of the various hydrocarbon series comprising the asphaltenes, resins, aromatics fraction, and saturates fraction (Chapter 9) give rise to much overlapping of fractions into neighboring series, both in molecular weight (Chapter 12) and in the hydrogen-to-carbon atomic ratio (Chapter 4, Fig. 14.2).

The asphaltenes have been proposed to be the final (excluding *carbenes* and *carboids*, those organic fractions of petroleum that are insoluble in toluene or benzene) (Fig. 14.3; Chapter 9) maturation products from the original protopetroleum. Oxidation experiments certainly indicate that the reaction sequence

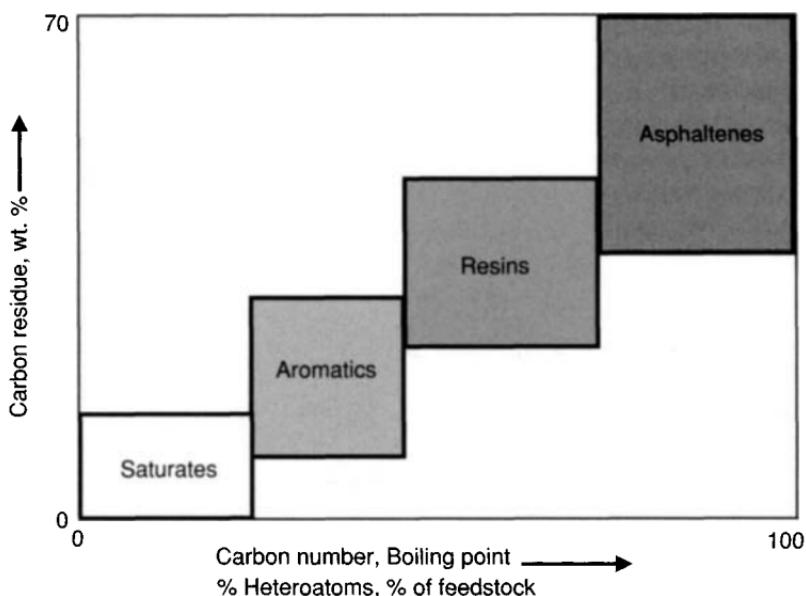


Figure 14.2. Carbon residue yields showing the overlap of various fractions.

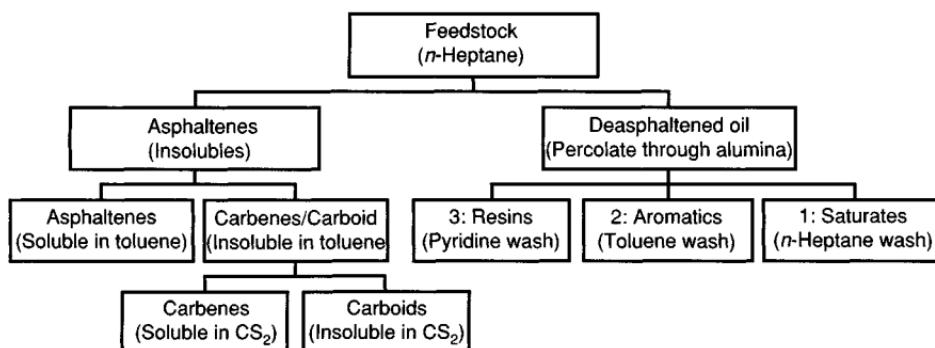
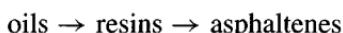


Figure 14.3. Feedstock fractionation.

is as follows (Moschopedis and Speight, 1976b):



Whether or not the maturation scheme is such a linear progression or a complex scheme of a variety of reactions is not known. A multistep reaction scheme for the formation of the petroleum constituents from the original protopetroleum is more likely, and it may also be considered just as probable that asphaltenes are formed simultaneously with the other constituents of petroleum (Speight, 1999). The conjecture is that a more complex reaction scheme than that indicated above is entirely possible, even likely, and it is not certain what role, if any, oxidation plays in maturation.

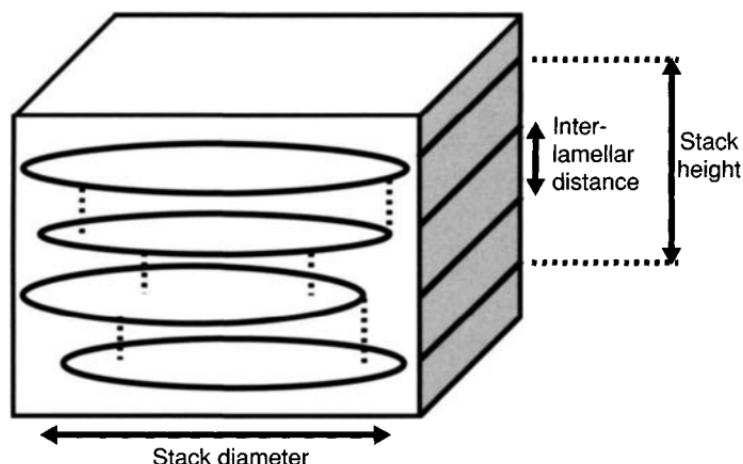
As indicated by the atomic hydrogen-to-carbon ratios (Chapter 4) as well as techniques such as carbon magnetic resonance spectroscopy (Chapter 7), a relatively high degree of aromaticity is generally prevalent in the asphaltenes and the resins. In some resins, however, the hydrocarbons show an increase in aliphatic material (more side chains, for example) until, with considerable saturation, the oils, which contain numerous alkyl chains of varying length, are reached. The degree of aromaticity is important when the resins are desorbed from a solid adsorbent (Chapter 9). A high aromaticity of the maltenes (i.e., that part of petroleum remaining after the asphaltenes have been removed, often referred to as the *deasphalted* or *deasphaltened* oil; Chapter 9) indicates good solvency for the asphaltenes. In fact, the solvent power of the maltenes is one of the most important factors in determining the physicochemical behavior of the petroleum colloid system (Speight, 1994; Sheu and Storm, 1995).

The means by which asphaltenes associate in solution and in crude oil has been the subject of many investigations, and much of the work related to asphaltene association has arisen from molecular weight measurements (Chapter 12).

Deductions have been made about the asphaltene micelle from such measurements, but there is still considerable conjecture about the true nature of the micelle. Specifically, there is some debate about whether the micelle in petroleum is composed of homogeneous material, that is, composed only of asphaltene molecules, or is composed of asphaltene and resin molecules (Pfeiffer and Saal, 1940; Dickie and Yen, 1967; Koots and Speight, 1975; Speight, 1994, 1999).

The means by which asphaltenes and resins interact in petroleum remains the subject of much discussion, but hydrogen bonding (Moschopedis and Speight, 1976a; Acevedo et al., 1985) and the formation of charge-transfer complexes (Yen, 1974) have been cited as the causative mechanisms, with a high degree of justification. Indeed, the influence of hydrogen bonding interactions in determining molecular structure is established (Taft et al., 1996), and to ignore the potential for hydrogen bonding interactions (as determined by infrared spectroscopy, Chapter 7) here would be a gross injustice. Finally, as a result of the various electrical properties of petroleum fractions (Chapter 6), there is also evidence that asphaltenes participate in charge-transfer complexes (Penzes and Speight, 1974; Speight and Penzes, 1978).

The original concept of the asphaltene-resin micelle invoked the concept of asphaltene-asphaltene association to form a graphitelike stack (Fig. 14.4) that acted as the micelle core that, in turn, was stabilized by the resins. Such data were derived from molecular weight measurement in nonpolar solvents followed by repeat determination in polar solvents (Chapter 12). Indeed, application of



is a polynuclear aromatic system.

..... dashed lines represent points of chemical/physical attraction..

Figure 14.4. Representation of graphitic stacking by asphaltene constituents.

methods such as X-ray diffraction methods (Chapter 7) to the study of asphaltenes aggregation has shown that the physical dimensions and shape of the aggregates are functions of the solvent used and the temperature of the investigation (Ravey et al., 1988; Overfield et al., 1989; Thiagarajan et al., 1995). In addition, surface tension measurements (Chapter 4) have been used to study the self-association of asphaltenes in pyridine and nitrobenzene (Sheu et al., 1992). A discontinuous transition in the surface tension as a function of asphaltene concentration was interpreted as the critical asphaltene concentration above which self-association occurs.

However, it must be recognized that the study of asphaltenes removed from petroleum might be analogous to studying a hard-boiled egg! The system has been denatured by the application of a physical technique. It is more reasonable to consider that the asphaltene constituents exist as aggregations only when separated and flocculated and that in the crude oil the micelle does not consist of aggregates of asphaltene molecules (Pelet et al., 1985; Speight, 1994). Solubility parameter calculations make it difficult to visualize the asphaltene constituents in petroleum as a graphitic stack, as suggested by X-ray diffraction (Chapter 7). The calculations indicate that instability (Chapter 13) could well be the outcome of the existence of such a graphitic stack.

When resins and asphaltenes are present together, hydrogen-bonding studies using infrared spectroscopy (Chapter 7) show that resin-asphaltene interactions are preferred over asphaltene-asphaltene interactions (Moschopedis and Speight, 1976a). If the same intermolecular forces are projected to petroleum, asphaltenes will exist in petroleum as single entities that are peptized, and effectively dispersed, by the resins. However, whatever the means by which the individual molecular species are included in the micelle, the structure is recognized as being complex (Bardon et al., 1996).

Therefore, petroleum is a complex system with each fraction (Chapter 9) dependent on other systems for complete mobility and solubility (Koots and Speight, 1975). If it can be presumed that the resins associate with the asphaltenes in the manner of an electron donor-acceptor through hydrogen bonding and /or through $\pi-\pi$ interactions, there could well be several points of structural similarity between the asphaltenes and resins that would have an adverse effect on the ability of the resins to associate with asphaltenes from a different crude oil (Koots and Speight, 1975; Moschopedis and Speight, 1976a).

An early hypothesis of the physical structure of petroleum (Pfeiffer and Saal, 1940) indicated that asphaltenes are the centers of micelles formed by adsorption or even by absorption of part of the maltenes, that is, resin material, onto the surfaces or into the interiors of the asphaltene particles (Fig. 14.5). Thus most of those substances with greater molecular weight and with the most pronounced aromatic nature are situated closest to the nucleus and are surrounded by lighter constituents of less aromatic nature. The transition of the intermicellar (dispersed

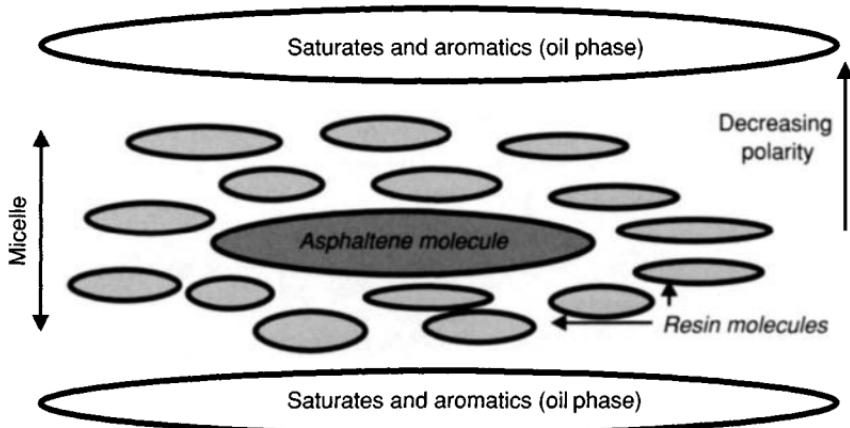


Figure 14.5. The original concept of petroleum structure.

or oil) phase is gradual and almost continuous. Continued attention to this aspect of asphaltene chemistry has led to the assumption that asphaltenes exist as clusters within the micelle. This arises mainly from the tendency for asphaltenes to associate in dilute solution in solvents of low polarity and from possible misinterpretation of viscosity data used to determine the molecular weight (Chapter 12; Moschopedis et al., 1976). The inferred presence of asphaltene *stacks* in the solid phase, as deduced from X-ray diffraction patterns (Chapter 7) (Dickie and Yen, 1967), also seemed to support the concept of the widespread existence of asphaltene clusters in the micelle.

The pronounced tendency of asphaltenes to form *aggregates* in hydrocarbon solution, as deduced from molecular weight measurement (Chapter 12), is one of their most characteristic traits. Thus, although a number of experimental methods indicate that isolated asphaltene monomers have an *average* molecular weight on the order of 1500–2500 (vapor pressure osmometry in polar solvents), numerous data show that asphaltenes associate spontaneously in most hydrocarbon media (Chapter 12), resulting in observed molecular weights of 10,000 or more. Thus it is not surprising that this tendency for asphaltenes to aggregate in hydrocarbon solvents has been applied to the existence of asphaltenes in crude oil. The debate is about whether or not this line of thinking is correct! Furthermore, there is evidence to suggest that when resins and asphaltenes are present together, there is preferential association between asphaltene constituents and resin constituents with little or no asphaltene-asphaltene and resin-resin association (Speight, 1999, 2000). Furthermore, if the composition and properties of the precipitated asphaltenes reflect those of the micelles in solution, the latter should be considered as mixed micelles.

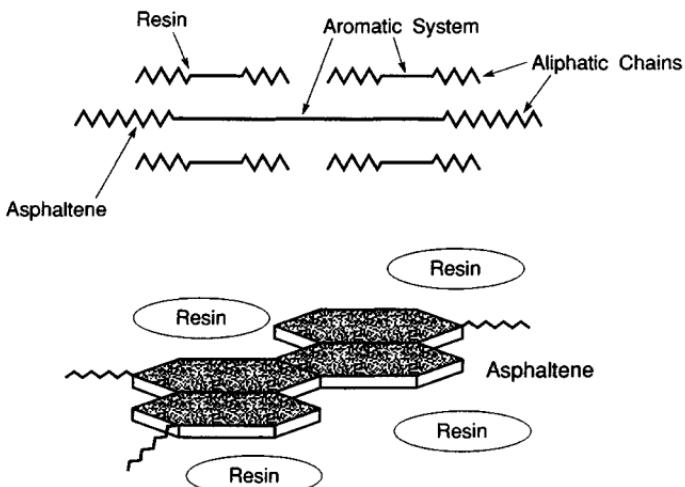


Figure 14.6. Representation of a micelle.

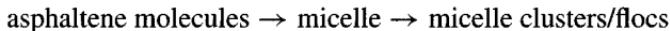
Asphaltene constituents vary in character, and resins are also complex mixtures of constituents (Chapter 9; Speight, 1999). Therefore, homogeneous micelles cannot be predicted.

Considering the micelles to be composed of asphaltene species that are peptized by resins and asphaltenes is a more reasonable approach. An important corollary of petroleum composition is that the mole fraction of resins is always larger than that of asphaltenes, and hence the micelles are expected to be richer in resins (Fig. 14.6). The micelle center would be formed from polar asphaltene molecules. These molecules would be surrounded by other more soluble asphaltene molecules, which would be placed between the center and the periphery. The inclusion of other asphaltene species is not seen as a graphite-type stack, as has been proposed previously. It is more likely an association of convenience that facilitates the association of the central asphaltene with resin species. In many cases, more than one asphaltene molecule per micelle is considered unlikely.

However, in such a model, the substances with higher molecular weights and with the most pronounced aromatic nature are situated closest to the nucleus and are surrounded by lighter constituents of less aromatic nature. The transition of the intermicellar (dispersed or oil) phase is gradual and almost continuous, because asphaltenes are incompatible with the oil fraction (Swanson, 1942; Koots and Speight, 1975), asphaltene dispersion is attributable mainly to the resins (polar aromatics).

Empirical observations indicate that the resins play an important role in stabilizing asphaltenes in crude oil (Koots and Speight, 1975 and references cited therein). Under unfavorable solvent conditions the asphaltene species are prone to

further aggregation into clusters that are unstable and precipitate from the crude oil (Chapter 9) (Mitchell and Speight, 1973; Koots and Speight, 1975; Yen, 1990).



This model requires that the asphaltene micelles be composed of an insoluble molecular core that associates with the resins, thereby providing steric stabilization against flocculation and precipitation. Thus the phase separation of asphaltenes on the addition of nonpolar solvents to the crude oil can be rationalized in terms of reduction of the solubility parameter or polarity of the hydrocarbon medium (Speight, 1992, 1994; Wiehe, 1992, 1993). This results in solubilization of the resins, leading to dissociation of the resin-asphaltene complexes, resulting a destabilization of the soon-to-be-unattended asphaltenes and flocculation/precipitation/phase separation.

The acceptance of these models and the concept of a micelle are easier to understand if the constituents of the resin and asphaltene fractions are viewed as two adjacent portions of a single broad compositional continuum (Chapter 9) that contains the polar, aromatic, and higher-molecular-weight components of petroleum. This allows the further acceptance of structural similarities in the asphaltenes and resins that facilitate formation of the asphaltene-resin micelle(s) (Speight, 1992, 1994, 1999).

On this basis, the stability of petroleum can be represented by a three-phase system in which the asphaltenes, the aromatic constituents (including the resins; Chapter 9), and the saturate constituents are delicately balanced (Speight, 1992, 1994, 1996). Various factors, such as oxidation, can have an adverse effect on the system, leading to instability or incompatibility as a result of changing the polarity, and bonding arrangements, of the species in crude oil in thermodynamic equilibrium (Cimino et al., 1995; Speight, 1999).

According to this model, the stabilization of the asphaltene micelles by the resin fraction derives from the contribution of the latter to the solvent power (polarity and aromaticity) of the medium. Destabilization of the asphaltenes, leading to phase separation, occurs when the solvating power of the medium toward the asphaltene monomers and micelles is reduced to the point at which they are no longer fully soluble.

The size of the asphaltene agglomerate varies as a function of the temperature, the asphaltene concentration, and the identity of the solvent (Chapter 12). This establishes that the self-association of the asphaltenes is reversible and that the molecular size in the solution state results from a true thermodynamic equilibrium between primary particles and reversible aggregates, the equilibrium constant depending on some property of the solvent. However, again, the correlation of the behavior of asphaltenes in hydrocarbon solvents to their behavior in crude oil is still speculative.

14.3. THE STABILITY/INSTABILITY OF THE CRUDE OIL SYSTEM

The original hypothesis of the physical structure of petroleum (Pfeiffer and Saal, 1940), in which resins played a role in the stabilization of the asphaltenes, and later confirmation of the role of the resins in petroleum (Swanson, 1942; Witherspoon and Munir, 1960; Koots and Speight, 1975) are supportive of this model.

This model envisions petroleum as a delicately balanced system insofar as the different fractions that contain hydrocarbons (saturates and aromatics) as well as heteroatom constituents (Fig. 14.7; Chapter 2). The heteroatom constituents tend to concentrate in the higher-molecular-weight fractions (the asphaltenes and resins). The nitrogen, oxygen, and sulfur species that are in near-neutral molecular locales will also occur in the saturates fraction and in the aromatics fraction, remembering that the nomenclature is not necessarily precise and that the composition of each fraction is a function of the separation process.

Separate, or insoluble, phases are produced when external effects perturb the system. Such effects might arise during recovery operations, during refining operations, or during storage resulting in the deposition of sludge or sediment (Chapter 13). Indeed, this is particularly true when circumstances permit phase separation (of asphaltenes or asphaltene-type material) from the oil medium, leading to the deposition of solids during recovery operations. Phase separation will

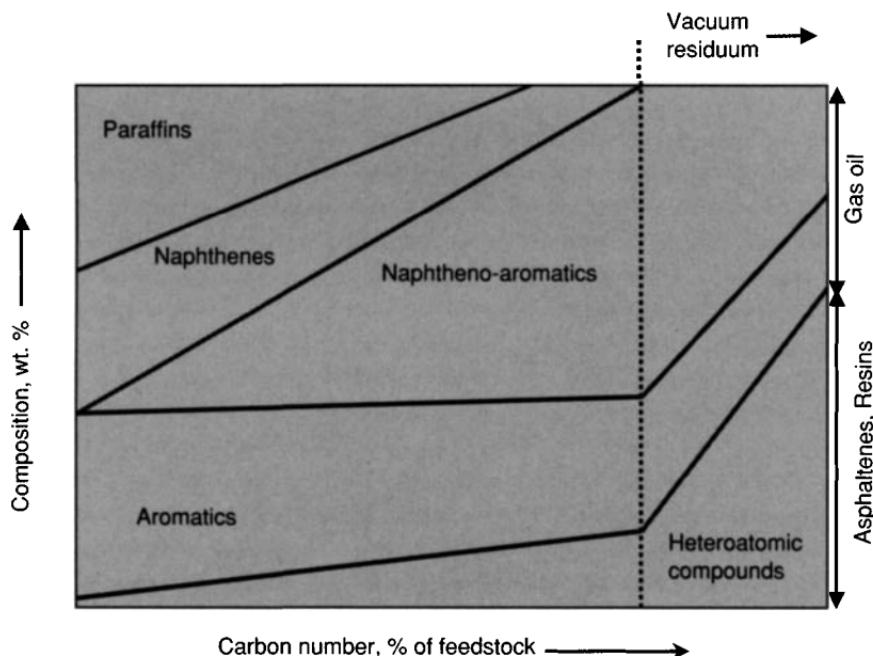


Figure 14.7. Representation of a feedstock showing hydrocarbon and heteroatom constituents.

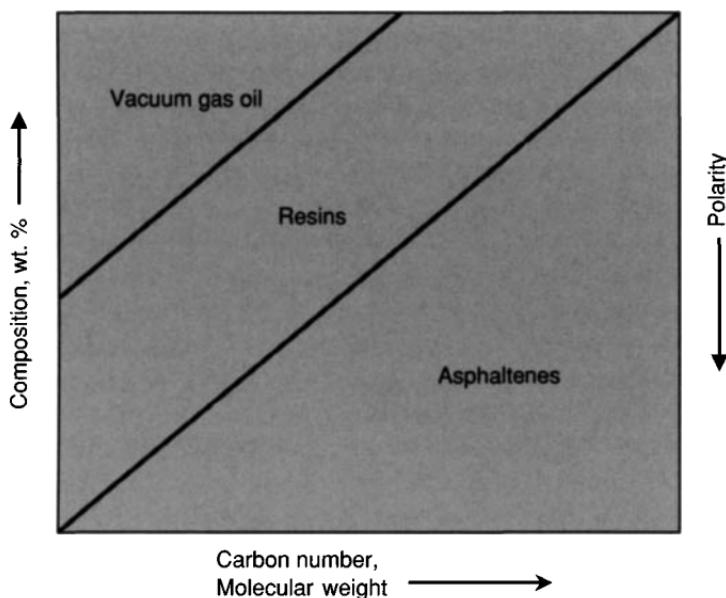


Figure 14.8. Asphaltene composition based on molecular weight and polarity.

cause coke formation during processing as well as failure of an asphalt pavement by loss of physical structure of the asphalt-aggregate system (Speight, 1992, 1994).

Asphaltenes are recognized as being a complex mixture of species of varying molecular weight and polarity (Fig. 14.8). Thus carbenes and carboids are lower-molecular-weight highly polar species that are predominantly products of thermal processes and might not occur in the typical asphaltenes fraction. However, the application of thermal techniques, such as fire flooding, to petroleum recovery can produce such species, and they will either deposit on the reservoir rock (Fig. 14.9) or appear as suspended solids in the oil. In fact, it is recognized that the polar species in the crude oil govern the oil-rock interactions in the reservoir (Bruning, 1991) from which many sediments (Chapter 13) can arise.

With the exception of the carbenes and the carboids, the fractions are compatible *provided* there are no significant disturbances or changes made to the system. Such changes are:

- the alteration of the natural abundance of the different fractions;
- the chemical or physical alteration of the constituents as might occur during recovery, especially changes that might be brought on by thermal processes;
- and
- alteration of the polar group distribution as might occur during oxidation by exposure to aerial oxygen during the recovery process.

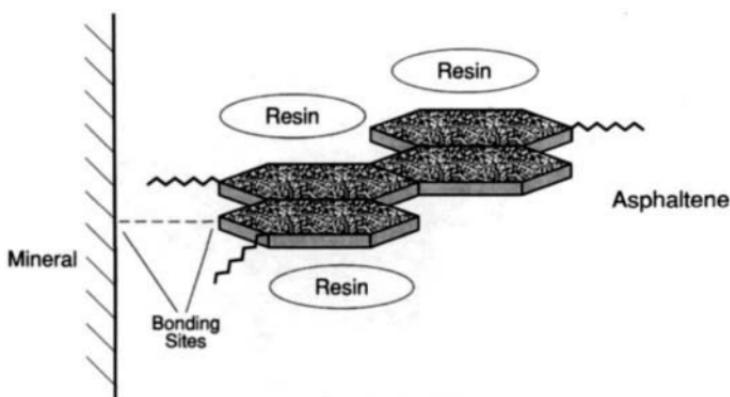


Figure 14.9. Perpendicular bonding of an asphaltene constituent to a rock or catalyst.

In the reservoir, asphaltene incompatibility can cause blockages of the pores and channels through which the oil must move during recovery operations (Park et al., 1994; Islam, 1994; Leontaritis, 1996).

All of these incidents cause disturbances in the petroleum system. However, when such disturbances occur, it is the higher-molecular-weight constituents that are most seriously affected, eventually leading to incompatibility (precipitation, sediment formation, sludge formation) depending on the circumstances. Thus the dispersability of the higher-molecular-weight constituents becomes an issue that needs attention, and one of the ways by which this issue can be understood is to be aware of the chemical and physical character of the higher-molecular-weight constituents. By such means, the issue of dispersability, and the attending issue of incompatibility, can be understood and even predicted.

The asphaltene fraction is chemically complex, but it can be conveniently represented on the basis of molecular weight and polarity (Fig. 14.8; Long, 1979, 1981). For different crude oils, the slope of the line representing the distribution of molecular weight and the variation in polarity will vary (Speight, 1994). Asphaltenes cannot be crystallized in the usual sense of the word. However, asphaltenes can be subfractionated by the use of a variety of techniques (Chapter 10). The fractions vary in molecular weight (Chapter 12) and in terms of the functional group types (Chapter 8) and functional group content (Francisco and Speight, 1984; Chapter 8).

In addition, any variation of the major parameters (precipitant, precipitant/oil ratio, time, and temperature) used to separate asphaltenes from the feedstock (Chapter 9) can cause substantial variations in the nature and amount of the separated asphaltenic material. It can vary from a dark brown amorphous solid to a black tacky deposit, either of which under the prevalent conditions could be termed an *asphaltene fraction*.

This has led to investigations to understand the structure and stability of crude oil, and one way in which this can be achieved is by an investigation of asphaltene precipitation/flocculation by titration using solvent/nonsolvent mixtures (Chapter 9). This may give an indication of both asphaltene and maltene (deasphaltened oil) properties (Heithaus, 1962; Bichard, 1969; Fuhr et al., 1991).

At the point of incipient precipitation, i.e., the point at which separation of asphaltenes from a crude oil becomes apparent (Chapter 9), the precipitated material is, presumably, a conglomeration of species based on molecular size and polarity of the types that constitute the asphaltenes (Long, 1979, 1981). This phenomenon has, however, also been addressed in detail and has helped increase the understanding of crude oil (asphaltene/maltene) relationships (Bestougeff and Darmois, 1947, 1948; Speight, 1971; Andersen and Speight, 1992; Speight, 1999 and references cited therein).

From molecular weight measurement (Chapter 12), it is evident that the nonasphaltene material is not conducive to formation of aggregates and, by inference, to the initiation of micelle formation, but it may have a positive surface excess due to polarity. Indeed, there is already evidence (Andersen and Birdi, 1991) that the nonasphaltene soluble fraction exerts no significant influence on the critical micelle concentration, but the data do not preclude the participation of the resins in the micelle. However, the resin constituents do not appear to be proactive in the formation of the micelle and might be regarded as inert in terms of micellization. Thus the occurrence of a micelle and a critical micelle concentration in the deasphaltened oil is certainly suspect, and such a concept might even be denied.

Petroleum is a continuum, and each component fraction depends on the other for stability of the whole oil. Also, it is the general consensus that the polar, i.e., heteroatom, constituents of petroleum are responsible for the formation of suspended organic solids during a variety of recovery processes (Islam, 1994; Park et al., 1994). However, an area that remains largely undefined, insofar as the chemistry and physics are still speculative, is the phenomenon of the incompatibility (Chapter 13) of the crude oil constituents, as might occur during these operations. The formation of a suspended solid phase during recovery (as well as during refining operations) is related to the chemical and physical structure of petroleum; the latter is greatly influenced by the former.

Asphaltenes and asphaltene-related-materials are known to deposit as sediments during recovery operations in the vicinity of production wells during miscible floods, after acid stimulation, or during pressure changes (Burke et al., 1990; Islam, 1994; Park et al., 1994). Many reservoirs produce without any such problems until the oil stability is perturbed during later stages of oil production.

The parameters that govern sediment formation (Chapter 13) and deposition of asphaltene materials from petroleum (Chapter 9) are related to the composition of the crude oil (Table 14.1) as well as the parameters used for the recovery process

Table 14.1. Relationship of Crude Oil Properties to Sludge and Sediment Formation

Property	Comments
Asphaltene content	Influences crude oil-rock interactions. Separates from oil when certain gases are dissolved. Thermal alteration causes dealkylation; formation of highly polar species.
Heteroatom species	Provide polarity in the crude oil. Preferential reaction with oxygen. Preferential thermal alteration.
Aromatic species	May be incompatible in paraffinic medium. Encourage flocculation.
Nonasphaltene constituents	Thermal alteration causes increased paraffinicity of oil medium; phase separation of polar species as sludge or sediment.

(Table 14.2). It must also be recognized that the material that deposits from the crude oil as a separate phase is more aromatic and richer in heteroatom compounds than the original crude oil. In fact, in some cases, especially when oxidation has occurred, the deposited material is more aromatic and richer in heteroatoms than the asphaltenes.

In terms of the crude oil parameters that influence sediment formation, there has been considerable focus on the asphaltene content as well as the chemistry and physics of the asphaltenes' relationship to the remainder of the oil. For example, although the asphaltene content of petroleum oils varies over a wide range (Koots and Speight, 1975), asphaltene content is not the single determining influence on sediment formation. It has been noted that asphaltene-to-resin ratios are usually below unity in oils that are stable and higher than unity in oils that exhibit ready precipitation of asphaltenic material (Sachanen, 1945). A word of caution is advised in the use of such ratios. The ratio is dependent on the relative amounts of asphaltenes and resins in the feedstock that are, in turn, dependent on the method of separation. One suspects that a clever circle of erroneous deduction is emerging!

Even though it is generally understood that asphaltene content of a crude oil increases with decreasing API gravity (Chapter 4), asphaltene precipitation (Chapter 9) has also been reported in light oils as well. Such an effect (gas deasphalting) arises from the increased solubility of hydrocarbon gases in the petroleum as reservoir pressure increases during maturation. Incompatibility (Chapter 13) will also occur when asphaltenes interact with reservoir rock, especially acidic functions of rocks, through the functional groups (e.g., the basic nitrogen species) just as they interact with adsorbents (Chapter 10). There is also the potential for asphaltene-rock interaction that is facilitated by a single functional group in which the remainder of the asphaltene molecule remains in the liquid phase (vertical

Table 14.2. Recovery Process Parameters and their Potential Adverse Effects Leading to Sludge and Sediment Formation

Property	Comments
Carbon dioxide injection	Lowers pH; can change oil composition, leading to phase separation of sludge or sediment and blocking of channels.
Miscible flooding	Hydrocarbon-rich gases lower the solubility parameter and solvent power of the oil and cause separation of asphaltene material.
Organic chemicals	Can lower the solubility parameter and solvent power of the oil and cause separation of asphaltene material; blocking of channels.
Acidizing	Interaction of crude oil constituents upsetting molecular balance and deposition of sludge or sediment; blocking of channels.
Pressure decrease	Can change composition of oil medium, leading to phase separation of asphaltene material as sludge or sediment; blocking of channels.
Temperature decrease	Can change composition of oil medium, leading to phase separation of asphaltene material as sludge or sediment; blocking of channels.

association relative to the rock surface) (Fig. 14.9). On the other hand, asphaltene-rock interactions can occur at several points of contact (horizontal association relative to the rock surface) (Fig. 14.10), thereby enhancing the bonding to the rock and, in some cases, affecting recovery operations to an even greater extent. Both modes of reaction can entrap other species (such as resins and aromatics) within the space between the rock and the asphaltene.

Another area in which incompatibility might play a detrimental role during recovery operations occurs as a result of aerial oxidation. The more polar species oxidize first with or without the presence of catalysts, leaving an oil that is relatively free of heteroatom species (Moschopedis and Speight, 1978). Thus oxidation is a means for the production of highly polar species in a hydrocarbon oil, leading to the deposition of polar sediments and being analogous to the deasphalting procedure. After incorporation of oxygen to an oil-dependent limit, significant changes occur to asphaltenes and resins. These changes are not so much caused by oxidative degradation as by the incorporation of oxygen functions that interfere with the natural order of intramolecular and intermolecular structuring leading to the separation of asphaltenic material (Moschopedis and Speight, 1976b; Moschopedis and Speight, 1977). Thus, with alterations in these parameters, sediment formation will occur but the nature of the sediment will vary and be dependent on the process

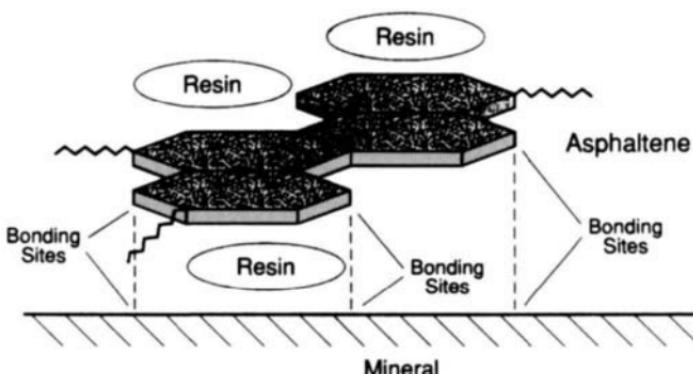


Figure 14.10. Horizontal bonding of an asphaltene constituent to a rock or catalyst.

of formation. There are also several process-related destabilizing forces that can cause precipitation of asphaltenic material, and each involves disturbance to the equilibrium that exists within petroleum.

For example, carbon dioxide causes the destabilization of the petroleum equilibrium by lowering pH, by changing oil composition, and by creating turbulence. Usually, asphaltene precipitation increases as the volume of carbon dioxide available to the crude oil increases during the later stages of carbon dioxide injection or stimulation. The most noticeable primary locations of asphaltene deposition are the wellbore and the pump regions. In addition, flooding of a rich gas (miscible flooding) destabilizes the asphaltene-crude oil mixture by lowering the solvent power of the solution. The hydrocarbon gases used in such applications effectively cause deasphalting (gas deasphalting, solvent deasphalting) of the crude oil. The negative effect of rich gas is at a maximum near the bubble point; this effect is alleviated after the bubble point is reached. Similarly, organic chemicals such as isopropyl alcohol, methyl alcohol, acetone, and even some glycol-, alcohol-, or surfactant-based solvents that do not have an aromatic component, may selectively precipitate asphaltenes and resins. Asphaltene precipitation may also be caused during well stimulation by acidizing. This causes a drastic shift in local chemical equilibria, pH, and liberation of carbon dioxide. It may also increase the concentration of some ions, such as iron, which will promote the formation of asphaltenic sediment.

A decrease in the pressure is another important factor that influences the onset of solids deposition from petroleum. In fact, the effect of pressure is particularly noticeable just above the bubble point for crude oils that are rich in light ends. Depending on the location of the pressure decrease, deposition may occur in different parts of the reservoir as well as in the wellbore and in the production stream. Furthermore, a decrease in pressure is usually accompanied by a decrease

in temperature that can also cause physicochemical instability leading to the separation of asphaltenic from the oil. Pressure change alone can also invoke similar asphaltene precipitation.

The asphaltene material in crude oil is electrically charged through the existence of zwitterions or polarization within the molecular species (Preckshot et al., 1943; Katz and Beu, 1945; Penzes and Speight, 1974; Speight and Penzes, 1978; Fotland and Anfinsen; 1996). Therefore, any process (such as the flow through reservoir channels or through a pipe) that can induce a potential across, or within, the oil will also result in the electrodeposition of asphaltene material through the disturbance of the stabilizing electrical forces. In addition, neutralization of the molecular charge will also result in the formation of sediment.

Two different models have been proposed to explain the behavior of petroleum and the potential for solids deposition during recovery operations (Kawanaka et al., 1989; Islam, 1994; Park et al., 1994).

The *continuous thermodynamic model* utilizes the theory of heterogeneous polymer solutions for predictions of the onset point and amount of organic deposits from petroleum crude. A *steric colloidal model* that is capable of predicting the beginning of organic deposition has also been developed. A combination of these two models results in a *fractal aggregation model*. These efforts have generally been adequate to predict the asphaltene-oil interaction problems (phase behavior and/or flocculation) wherever they may occur during oil production and processing.

In the continuous thermodynamic model, the degree of dispersion of the high-molecular-weight organic constituents in petroleum depends on the chemical composition of the petroleum. Precipitation of the high-molecular-weight material can be explained by a change in the molecular equilibria that exist in petroleum through a change in the balance of oil composition. Moreover, the precipitation process is considered to be reversible. Indeed, the reconstitution of petroleum after fractionation has been demonstrated (Koots and Speight, 1975) and lends support to this model.

The ratio of polar to nonpolar molecules and the ratio of high- to low-molecular-weight molecules in a complex mixture such as petroleum are the two factors primarily responsible for maintaining mutual solubility. The stability of the system is altered by the addition of miscible solvents causing the high-molecular-weight and/or polar molecules to separate from the mixture either in the form of another liquid phase or as a solid precipitate. Hydrogen bonding and the sulfur- and /or nitrogen-containing segments of the separated molecules could start to aggregate (or polymerize) and, as a result, produce a solid phase that separates from the oil.

In the steric colloidal model, the high-molecular-weight materials in petroleum are considered to be solid particles of different sizes suspended colloidally in the oil and stabilized by other petroleum constituents (i.e., resins) adsorbed on their surface. In the fractal aggregation model, it is assumed that $\pi-\pi$ interactions are

the principal means by which asphaltenes associate. This assumption may not be completely valid because of the observation that asphaltene-resin interactions may predominate over asphaltene-asphaltene interactions in petroleum (Speight, 1999). The concept that asphaltene-asphaltene interactions may be the predominant interactions is true for solutions of asphaltenes in hydrocarbon solvents as deduced from molecular weight data (Speight et al., 1985). However, there is no guarantee that these interactions are predominant in petroleum (especially with evidence that indicates the high potential for other interactions) (Speight, 1994, 1999).

Because the issue of the deposition of asphaltenic materials problem is complex, it is necessary to attempt an understanding of the deposition mechanism before an accurate and representative model can be formulated. Utilization of kinetic theory of fractal aggregation has enabled the development of the fractal aggregation model. This model allows us to describe properly several situations, such as phase behavior of heavy organic deposition, the mechanism of the association of the high-molecular-weight constituents, the geometric aspects of aggregates, the size distribution of the sediments, and the solubility of the high-molecular-weight constituents in the solution under the influence of a miscible solvent.

Another potential model involves use of the *solubility parameter* of the asphaltenes and the surrounding medium. It is known that the solubility of asphaltenes varies with the solubility parameter of the surrounding liquid medium (Mitchell and Speight, 1973), and calculation or estimation of the solubility parameters of various liquids is known. From these data, it is possible to estimate the point at which asphaltenic material is precipitated when the composition of the oil is changed by the addition of a hydrocarbon liquid (Mitchell and Speight, 1973). In fact, the solubility parameter has been used successfully to determine the character of heavy oils and investigate the separation of asphaltenic material (Wiehe, 1996). The solubility parameter concept also recognizes the gradation of polarity of the asphaltenes as selective precipitation occurs during the addition of a nonsolvent when the most polar constituents are precipitated first (Andersen and Speight, 1992).

The models that apply the solubility parameter concept calculate the interaction through an assumption of the total crude oil as formed by asphaltenes and deasphaltened oil; hence the system is regarded as a two-component system. The changes in phase equilibrium are caused by the changes in the solubility parameter of either of the two pseudo-components, which may happen either by dissolution of gas or alkane in the deasphaltened oil phase or by changes in temperatures. The amount of precipitated asphaltenes is calculated as the differences in asphaltenes present in the oil and the solubility of asphaltenes at the saturation point. In the different models the change in the composition of the deasphaltened oil is taken as significant for the phase equilibrium, and various methods, i.e., cubic equations of state, are applied to determine the properties of this fraction.

Further development of this concept (Speight, 1994) has led to the graphical representation of the solubility parameters of polynuclear aromatic systems and

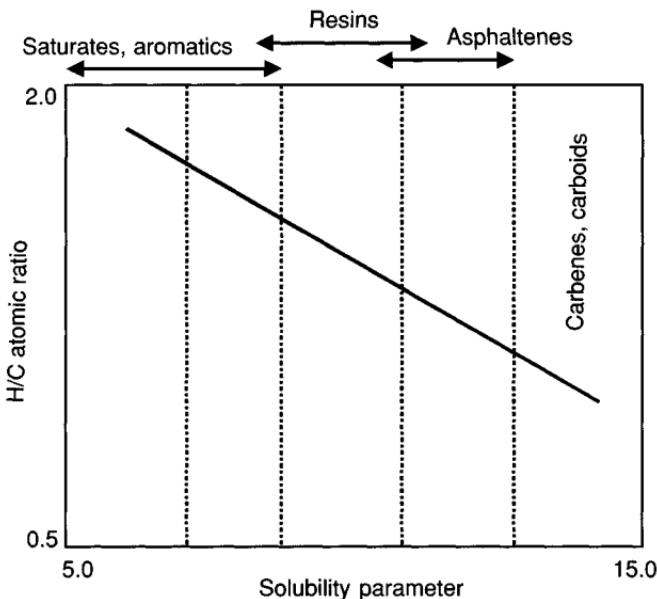


Figure 14.11. Atomic hydrogen-to-carbon ratio and solubility parameter.

estimation of the solubility parameter of the asphaltenes based on hydrogen-to-carbon ratios (Fig. 14.11). Further development of this knowledge can allow the progress of asphaltene deposition to be followed and the region of sediment formation (or the region of instability and incompatibility) to be estimated using a simplified phase diagram (Fig. 14.12).

In general, these models are, to a degree, applicable to the prediction of heavy organic deposition (asphaltene, paraffin/wax, resin) from petroleum caused by changes in pressure, temperature, and composition. However, the use of assumptions that do not reflect, or recognize, what might be the actual chemical and physical structure of petroleum can lead to errors in the data. Further modeling must involve recognition of the more modern concepts of the structure of petroleum as well as application of the models to the predictability of the location and amount of the deposition of the sediments inside the producing wells and oil-transport pipelines.

Thus petroleum instability reflected by asphaltene separation or precipitation or the mere presence of asphaltenes may invoke many implications in the behavior of petroleum during recovery and refining operations. Asphaltene separation or precipitation may occur under various thermally or nonthermally enhanced oil recovery schemes or even primary production conditions.

These models are proposed as being applicable to the prediction of sediment (i.e., asphaltene, resin, wax) formation and deposition from petroleum due to changes in pressure, temperature, and composition. Further modeling must involve

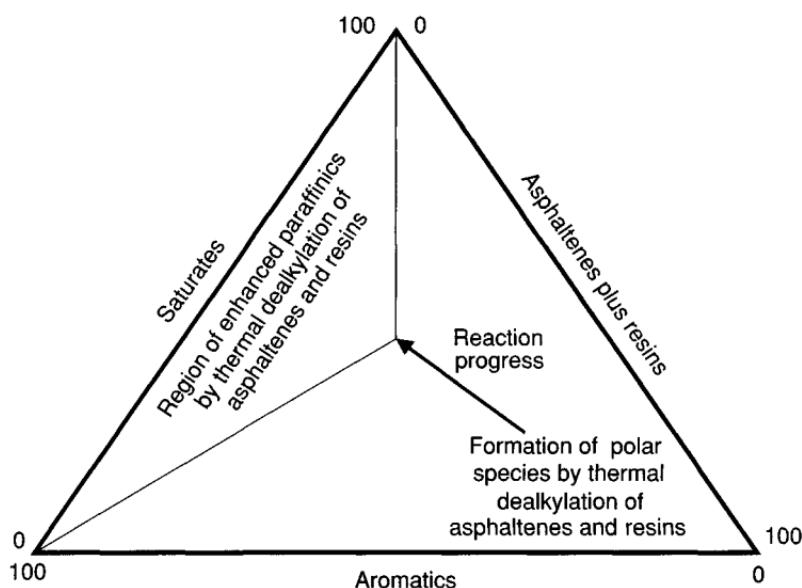


Figure 14.12. Phase relationships during thermal reactions.

an understanding of the chemistry of these materials and reflect the more modern approach to the physicochemical structure of petroleum. Only then will it be possible to more correctly predict the onset of precipitation as well as the location and amount of the sediment deposition in the producing wells and in oil-transport pipelines. Such is the subject of the next chapter (Chapter 15).

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CHAPTER

15

USE OF THE DATA—MAPPING AND PREDICTABILITY

15.1. INTRODUCTION

The data derived from any one or more of the evaluation techniques described here give an indication of the characteristics of as well as an indication of the means by which the crude feedstock should be processed as well as of the prediction of product properties (Dolbear et al., 1987; Adler and Hall, 1988; Wallace and Carrigy, 1988; Al-Besherah et al., 1989; Speight, 1999, 2000 and references cited therein). Other properties may also be required for more detailed evaluation of the feedstock and for comparison between feedstocks even though they may not play any role in dictating which refinery operations are necessary for processing.

However, to proceed from the raw evaluation data to full-scale production is not the preferred step; further evaluation of the processability of the feedstock is usually necessary through the use of a pilot-scale operation. To take the evaluation of a feedstock one step further, it may then be possible to develop correlations between the data obtained from the actual plant operations (as well as the pilot plant data) with one or (preferably) more of the physical properties determined as part of the initial feedstock evaluation. It may also be necessary to use kinetic profiles developed from a variety of thermal experiments (Gray, 1994). Such methods are beyond the scope of this book and are not included here.

Early attempts at evaluating a feedstock involved the use of simple formulae based on the correlation of one of more physical properties with behavior (Speight, 1999, 2000). For example, the relationship of carbon residue (Chapter 5) to actual coke yield and the yield of other products was established for a variety of feedstocks (Table 15.1). This technique has been fine-tuned to accommodate the larger variety of feedstocks that are now available for refineries (see, e.g., Roberts, 1989; Schabron and Speight, 1997a, 1997b).

Furthermore, it is not only the *conventional* physical properties that have been used for feedstock evaluation. For example, evaluation of feedstocks from physical properties may also be achieved by use of the refractivity intercept (Chapter 6). Thus, if refractive indices of hydrocarbons are plotted against the respective density, straight lines of constant slope are obtained, one for each homologous series;

**Table 15.1. Estimation of Product Yields
for Delayed Coking**

Wilmington	
Coke, wt%	= $39.68 - 1.60 \times ^\circ\text{API}$
Gas ($\leq \text{C}_4$), wt%	= $11.27 - 0.14 \times ^\circ\text{API}$
Gasoline, wt%	= $20.5 - 0.36 \times ^\circ\text{API}$
Gas oil, wt%	= $28.55 + 2.10 \times ^\circ\text{API}$
Gasoline, vol%	= $\left(\frac{186.5}{131.5 + ^\circ\text{API}} \right)$ (gasoline, wt%)
Gas oil, vol%	= $\left(\frac{155.5}{131.5 + ^\circ\text{API}} \right)$ (gas oil, wt%)
East Texas	
Coke, wt%	= $45.76 - 1.78 \times ^\circ\text{API}$
Gas ($\leq \text{C}_4$), wt%	= $11.92 - 0.16 \times ^\circ\text{API}$
Gasoline, wt%	= $20.5 - 0.36 \times ^\circ\text{API}$
Gasoline, vol%	= $\left(\frac{186.5}{131.5 + ^\circ\text{API}} \right)$ (gasoline, wt%)
Gas oil, vol%	= $\left(\frac{155.5}{131.5 + ^\circ\text{API}} \right)$ (gas oil, wt%)

the intercepts of these lines with the ordinate of the plot are characteristic, and the refractivity intercept (page 171) is derived from the formula:

$$\text{refractivity intercept} = n - d/2$$

The intercept cannot differentiate accurately among all series, which restricts the number of different types of compounds that can be recognized in a sample. The technique has been applied to nonaromatic olefin-free materials in the gasoline range by assuming additivity of the constant on a volume basis. Further manipulation of the formula and data allows derivation of an equation that is applicable to straight-run lubricating distillates if the material contains between 25 and 75% of the carbon present in naphthenic rings:

$$\text{refractivity intercept} = 1.0502 - 0.00020\% \text{C}_N$$

Obviously, this may be of little use in the modern refinery because of the scarcity of straight-run lubricating distillates, especially those containing the requisite proportion of naphthenic carbon (Chapter 2). Other formulae using the refractive index (RI) (Chapter 6) and properties such as specific gravity (SG) (Chapter 4) and molecular weight (MW) (Chapter 12), have also been developed (Table 15.2; Dhulesia, 1986).

Indeed, the use of physical properties for feedstock evaluation has continued in refineries and in process research laboratories to the present and will continue

Table 15.2. Correlations for Various Physical Properties

Aromatic Carbon Content:

$$\text{CA} = -814.136 + 635.192 \times \text{RI}(20) - 129.266 \times \text{SG} + 0.1013 \\ \times \text{MW} - 0.340 \times \text{S} - 6.872 \times \ln(\nu)$$

Hydrogen Content:

$$\text{H}_2 = 52.825 - 14.26 \times \text{RI}(20) - 21.329 \times \text{SG} - 0.0024 \\ \times \text{MW} - 0.052 \times \text{S} + 0.757 \times \ln(\nu)$$

Molecular Weight:

$$\text{MW} = 7.8312 \times 10^{-3} \times \text{SG}^{-0.0976} \times \text{AP}_{^{\circ}\text{C}}^{0.1238}$$

Refractive Index @ 20°C:

$$\text{RI}(20) = 1 + 0.8447 \times \text{SG}^{1.2056} \times (\text{VABP}_{^{\circ}\text{C}} + 273.16)^{-0.0557} \times \text{MW}^{-0.0044}$$

Refractive Index @ 60°C:

$$\text{RI}(60) = 1 + 0.8156 \times \text{SG}^{1.2392} \times (\text{VABP}_{^{\circ}\text{C}} + 273.16)^{-0.0576} \times \text{MW}^{-0.0007}$$

for some time. It is, of course, a matter of choosing the relevant and meaningful properties to meet the nature of the task.

However, the emphasis on feedstock evaluation has taken a turn in the direction of feedstock mapping. 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 supercede 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.

Not all of the feedstock mapping procedures that have been cited can be discussed here. Each process chemist, process engineer, and refiner has his/her own preferences, and such efforts are feedstock dependent as well as being refinery dependent. It is, in fact the purpose of this chapter to introduce the reader to the potential that exists in this area of science and engineering. 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).

This chapter will merely serve as an introduction to feedstock mapping and the consequences of such efforts. In fact, this final chapter may be considered as an epilog that is not the end but, in reality, the beginning of the beginning!

15.2. FEEDSTOCK MAPPING

Feedstock fractionation (Chapter 9) has played a significant role, along with the physical testing methods, in evaluating petroleum as a refinery feedstock. For

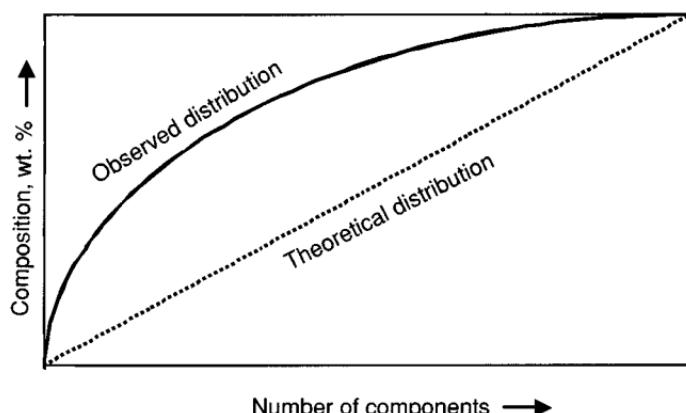


Figure 15.1. Hydrocarbon distribution in a crude oil.

example, distillation, being the simplest form of fractionation, has been and continues to be used as a means of describing a feedstock in the form of a distillation profile (Chapter 5). Early investigations showed that petroleum did not contain all possible isomers of the various hydrocarbons but contained preferential isomers (Fig. 15.1). In this very simple *map*, the actual constituents were shown again the theoretical constituents in a line profile. This allowed refiners to be prepared for a more specific variety of straight-run hydrocarbon products than had previously been thought.

Later distillation profiles were a little more detailed insofar as the profile showed the distillation yields as a line that continued into the vacuum range as atmospheric equivalent boiling points (Chapter 5) whether in two dimensions (Fig. 15.2) or in three-dimensional form (Altgelt and Boduszynski, 1994). In addition, profiles could be compared for different feedstocks (along with other properties) (Fig. 15.3) that allowed comparison and rationalization of refining behavior for different crude oils. Elemental compositions (Chapter 4) were also part of the distillation profile (Fig. 15.4). Such information could be as detailed or as brief as the process chemist/process engineer/refiner dictated.

At the same time, and as feedstock quality changed, the hydrogen content (Chapter 4) and molecular weight (Chapter 12) were considered to be important parameters and worth mapping as a match to other properties, such as nitrogen content (Chapter 4) and viscosity (Chapter 4) (Fig. 15.5). In many cases, the properties were inserted on the correct numbered scale as one of the map coordinates.

The reason for the importance of the hydrogen content (Chapter 4) and the molecular weight (Chapter 12) is that both are used to give an evaluation of the feedstock in terms of the hydrogen required to upgrade the feedstock to specific products. In addition, nitrogen content (Chapter 4) indicates not only the

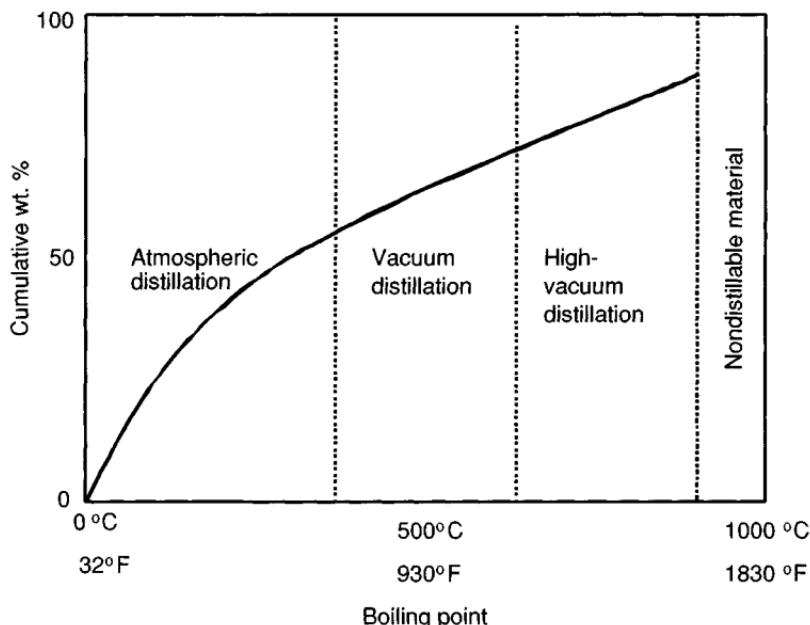


Figure 15.2. A distillation profile (true boiling point curve) of a crude oil.

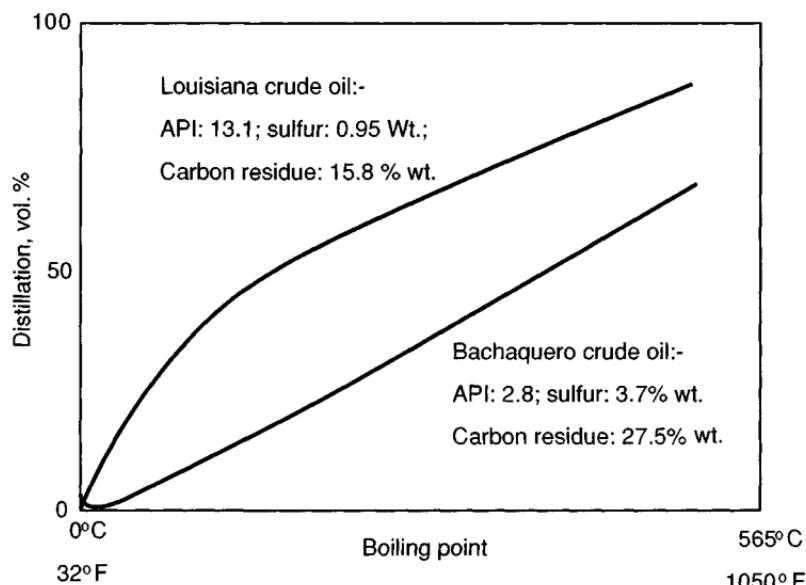


Figure 15.3. Distillation profiles and other physical properties for two crude oils.

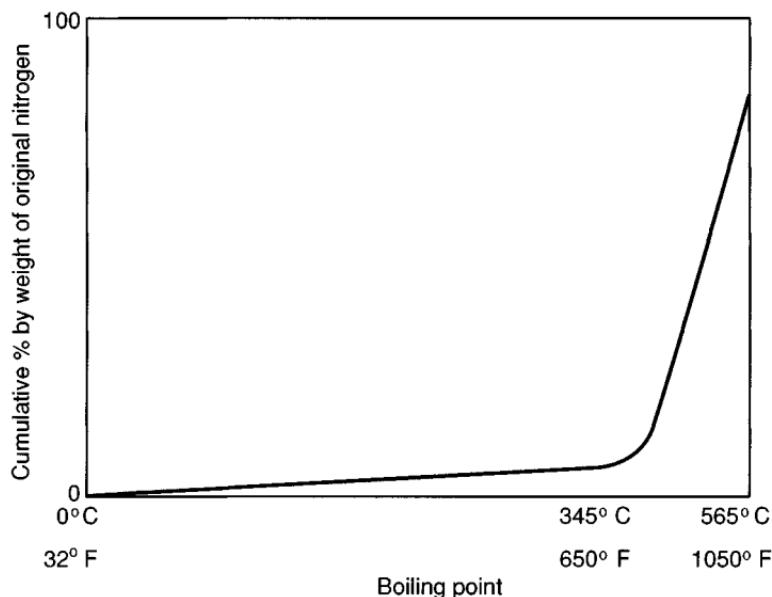


Figure 15.4. Nitrogen content and a distillation profile.

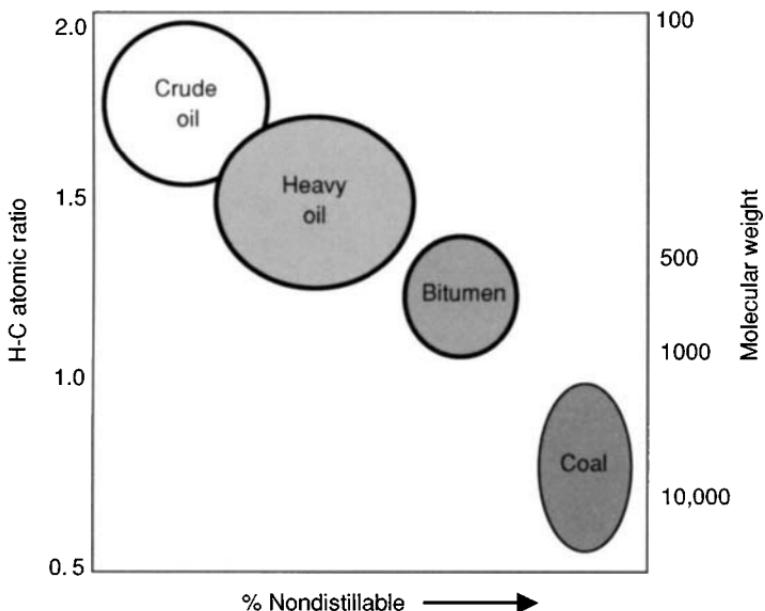


Figure 15.5. Atomic hydrogen-to-carbon ratios and molecular weights.

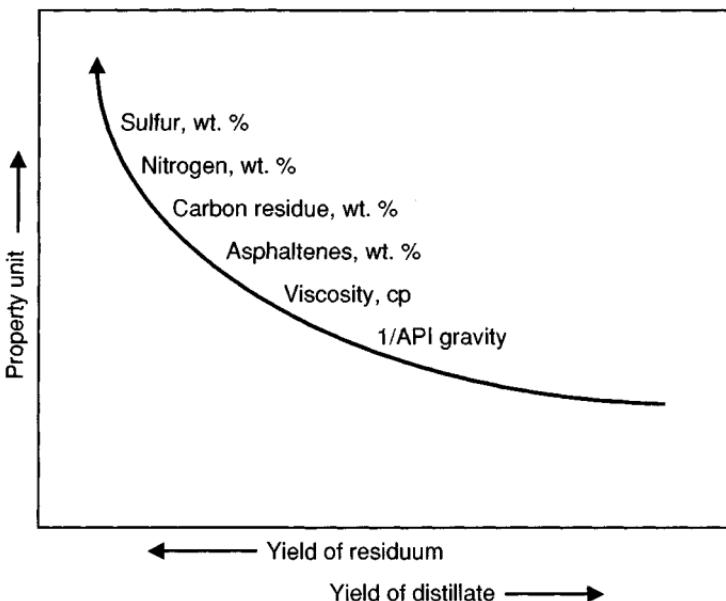


Figure 15.6. Residuum yield and physical property variation.

hydrogen required to remove it as ammonia but also the type of catalyst necessary for processing. Viscosity (Chapter 4) is an indicator of the ability of the feedstock to flow or, more correctly, to resist flow. Other properties such as pour point (Chapter 5) (Fig. 15.6) were also used to predict feedstock behavior in a refinery. A combination of viscosity (Chapter 4), API gravity (Chapter 4), and temperature (Fig. 15.7) also presented indications of behavior in a refinery as well as the ability of the material to flow in a reservoir. Indeed, pour point (Chapter 5) and reservoir temperature are the best gauge of fluidity and flow in a reservoir.

One of the early findings of composition studies (Chapter 9) was that the behavior and properties of any material are dictated by composition (Speight, 1999, 2000 and references cited therein). Although the early studies were primarily focused on the composition and behavior of asphalt, the techniques developed for those investigations have provided an excellent means of studying heavy feedstocks (Altgelt and Boduszynski, 1994; Speight, 1999, 2000). Later studies have focused not only on the composition of petroleum and its major operational fractions but also on further fractionation (Chapter 9), which allows different feedstocks to be compared on a relative basis to provide a very simple but convenient feedstock map.

Thus it is not surprising that one of the most effective means of feedstock mapping has arisen through the use of fractionation methods (Chapter 9) in which

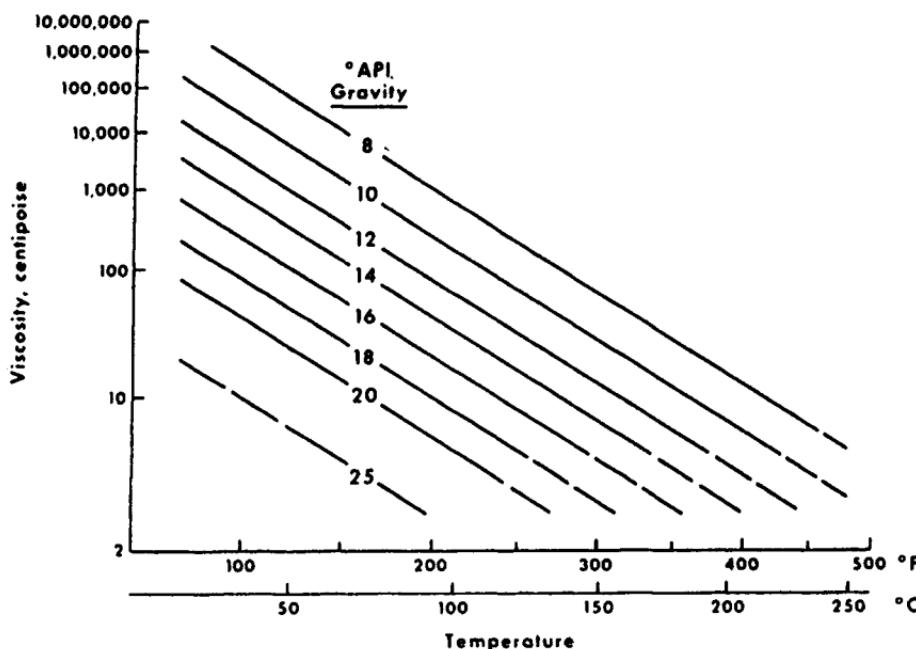


Figure 15.7. API gravity, viscosity, and temperature profiles.

the feedstock is subdivided into several fractions by standard procedures (e.g., Fig. 15.8). The simplest map that can be derived from such methods shows the feedstock as a three-phase system based on asphaltene separation (Fig. 15.9). Indeed, the asphaltenes themselves can be differentiated on the basis of the solubility parameter of the solvent or solvent used for the separation (Figs. 15.10 and 15.11; Mitchell and Speight, 1973).

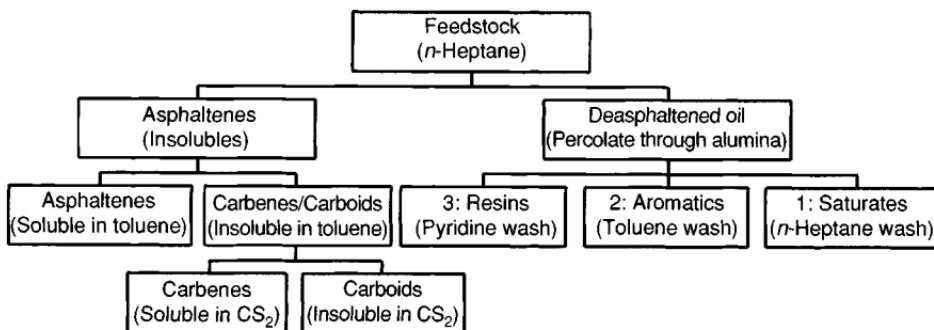


Figure 15.8. Feedstock fractionation.

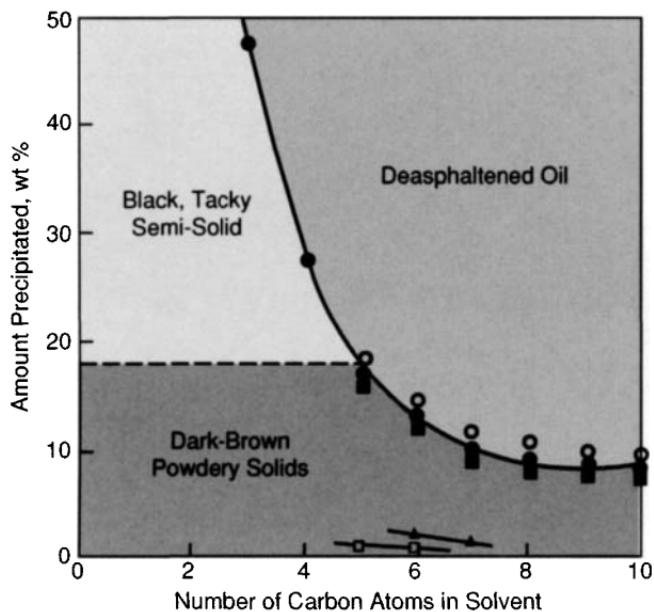


Figure 15.9. Three-phase diagram for crude oil.

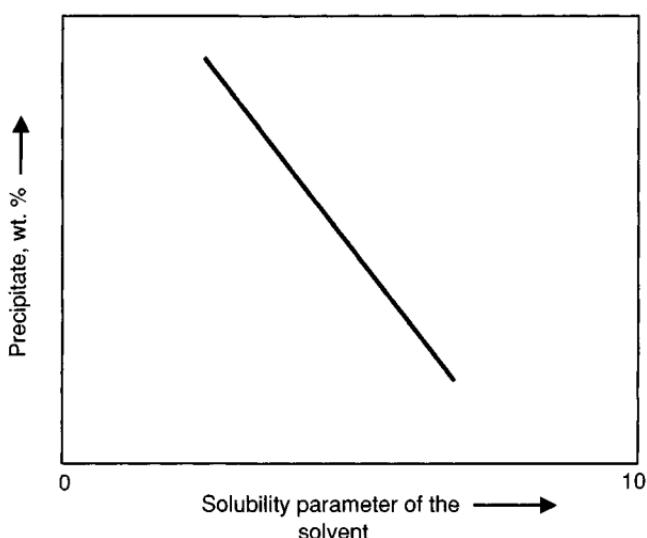


Figure 15.10. Asphaltene yield and solubility parameter.

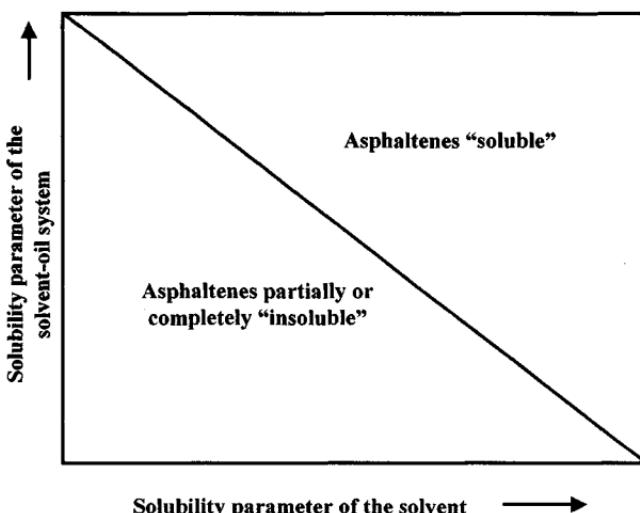


Figure 15.11. Two-phase diagram for crude oil.

The whole feedstock can be mapped as a series of boxes equivalent to each fraction with the saturates fraction and the aromatics fraction combined as a single fraction (Fig. 15.12) or shown separately according to boiling range (Fig. 15.13) (Corbett and Petrossi, 1978; Speight, 1999, 2000). In this manner, various feedstocks can be mapped and compared to the parent feedstock. Furthermore, by careful selection of an appropriate technique it is possible to obtain a detailed overview of feedstock or product composition (Fig. 15.14) that can be further subdivided into specific compound types within the feedstock (Fig. 15.15) or on the basis of an envelope that is constructed from carbon and number and boiling point (Fig. 15.16) that allows cut-points to be made that illustrate the relative positions of the atmospheric residuum and the vacuum residuum (Fig. 15.17) as well as very general (often not too accurate) predictions of the relative distillate and coke forming propensity (Fig. 15.18). Placing lines on such maps for asphaltenes and resin fraction is somewhat difficult because of the complexity of these fractions and the basis of polarity and molecular weight as the determinant for the resin and asphaltene fractions. Nevertheless, these maps are moving closer to use as a means of process predictability.

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 they do allow predictions of feedstock behavior. It must also be recognized that such a representation varies for different feedstocks.

Thus, by careful selection of an appropriate technique, it is possible to obtain an overview of petroleum composition that can be used for behavioral predictions.

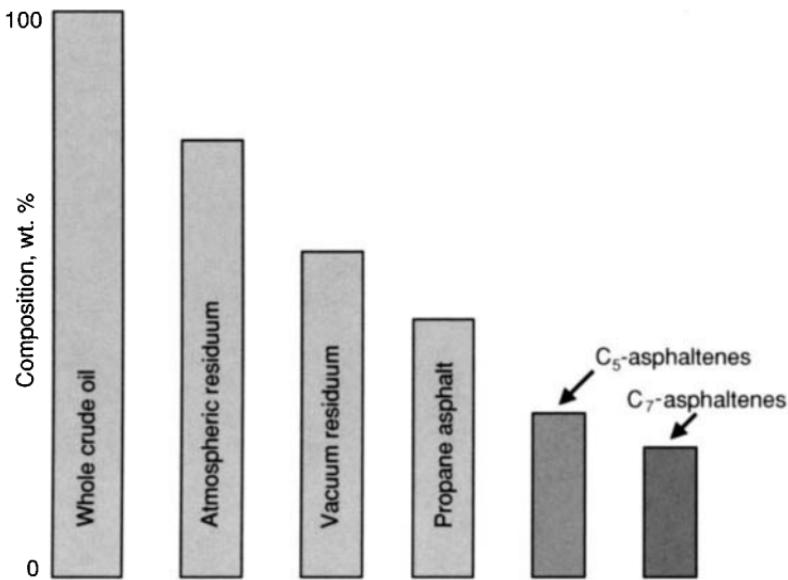


Figure 15.12. Relationship of feedstock fractions.

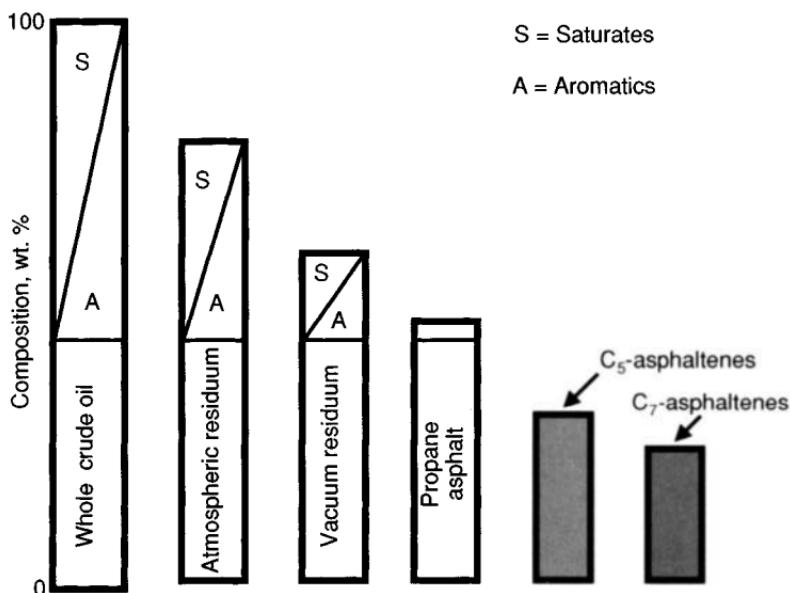


Figure 15.13. Fractionation showing saturates and aromatics fractions.

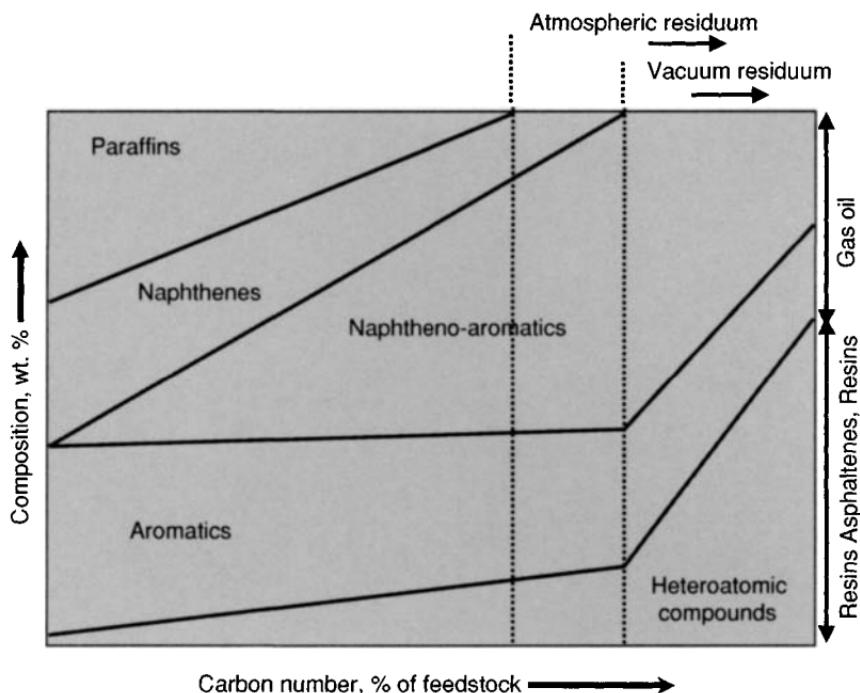


Figure 15.14. A fractionation map.

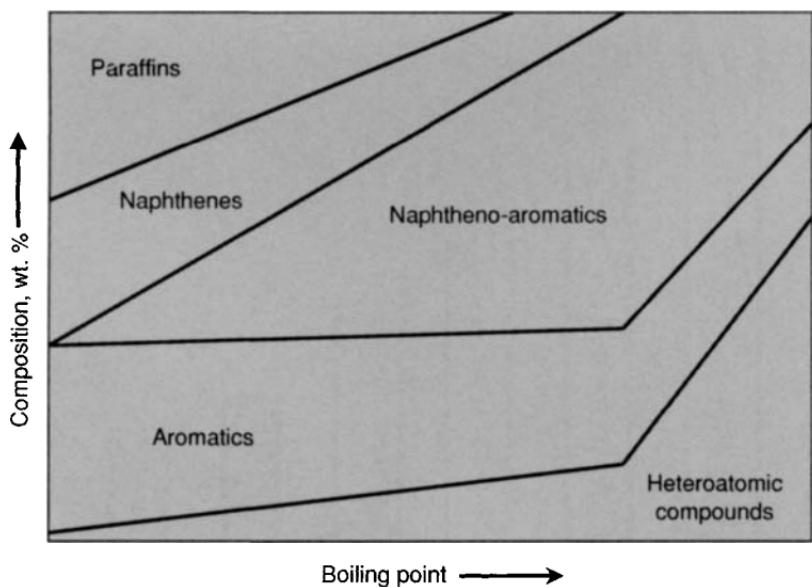


Figure 15.15. A compound-type fractionation map.

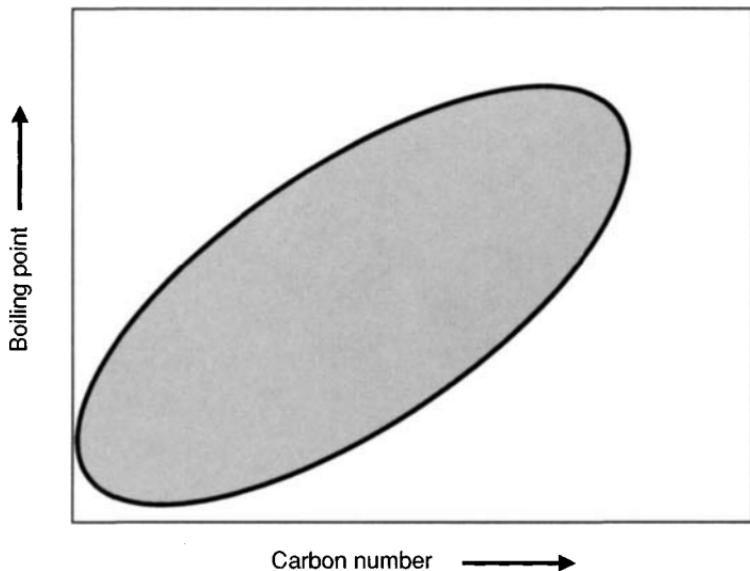


Figure 15.16. A boiling point-carbon number map.

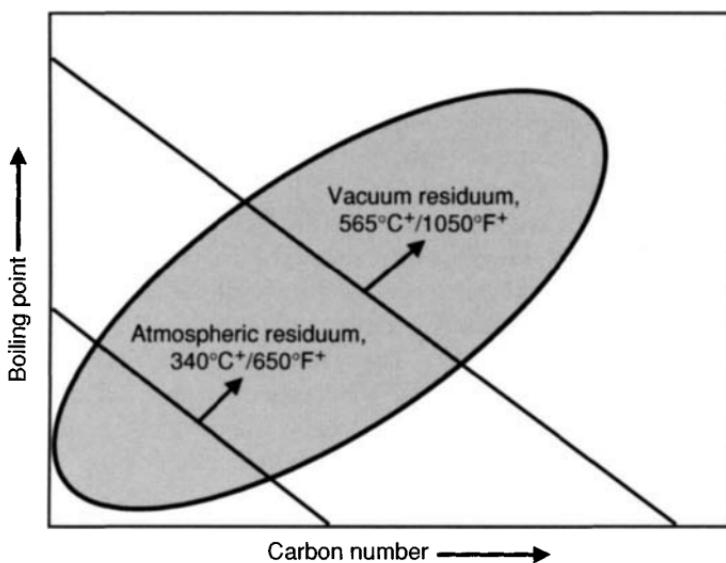


Figure 15.17. A boiling point-carbon number map showing residua cut-offs.

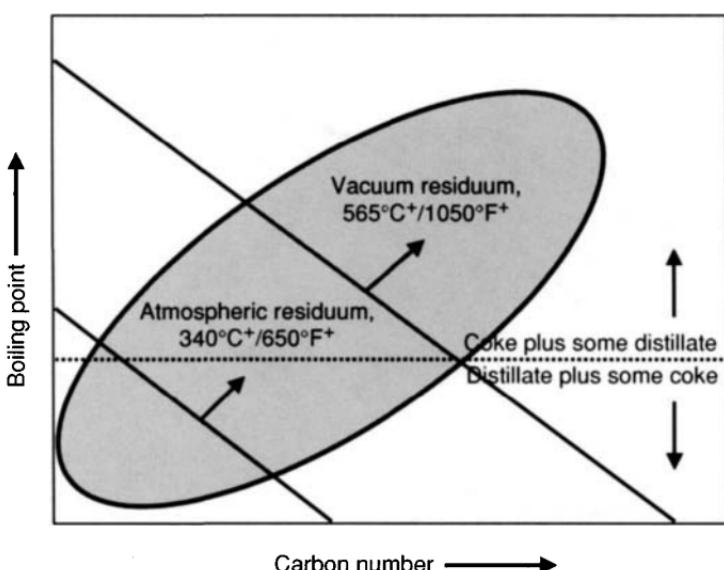


Figure 15.18. A boiling point–carbon number map showing carbon residue trends.

By taking the approach one step further and by assiduous collection of various subfractions, it becomes possible to develop the petroleum map and add an extra dimension to compositional studies. Petroleum and heavy feedstocks then appear more as a continuum than as four specific fractions. For example, and to continue the concept that petroleum can be represented as a three-phase system, using various data such as composition or solubility parameter, the feedstock can be shown as a simple system that changes during to the formation of an insoluble phase as thermal reactions proceed (Fig. 15.19). Application of precise numbers to such a map allows more accurate predictions. There is even the possibility of adding a third dimension to such a map, thereby enhancing predictability.

Such a concept has also been applied to the asphaltene fraction (Chapter 9), in which asphaltenes are considered a complex state of matter based on molecular weight and polarity (Long, 1981). The advantage of such a concept is that it can be used to explain differences in asphaltene yield with different hydrocarbons (pentane and heptane) and also differences in the character of asphaltenes from the thermal degradation products, such as carbenes and carboids (Fig. 15.20). Further work using high-performance liquid chromatography (Chapter 10) has allowed mapping of the asphaltene reaction that confirms the range and distribution of molecular types (Fig. 15.21) with different asphaltene fraction giving different chromatographic profiles (Fig. 15.22) (Speight, 1994, 1999).

At this point, mapping the deasphalting process has been practiced for some time (Flynn et al., 1961; Ditman, 1973). This concept simply measures the amount

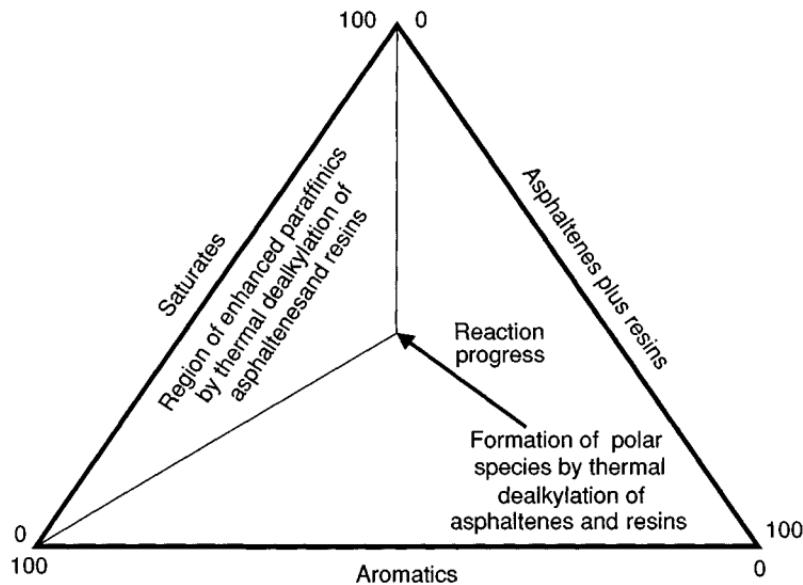


Figure 15.19. Crude oil as a three-phase system with instability region.

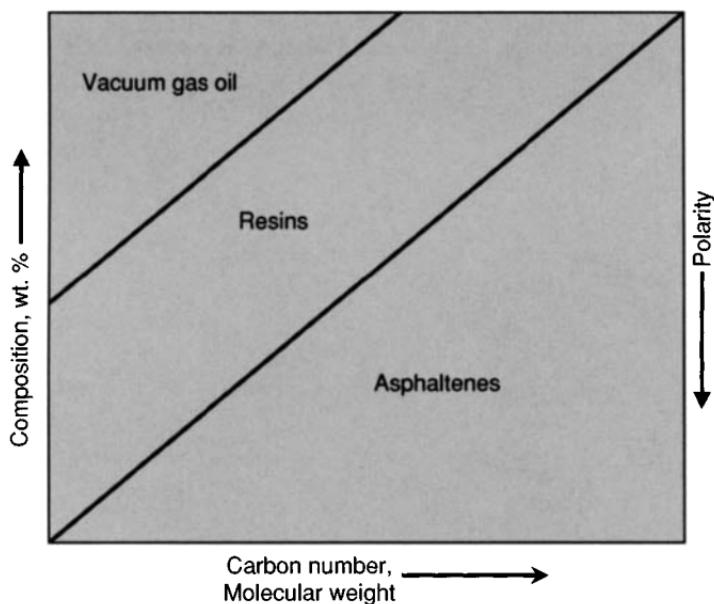


Figure 15.20. Molecular weight-polarity representation of asphaltenes.

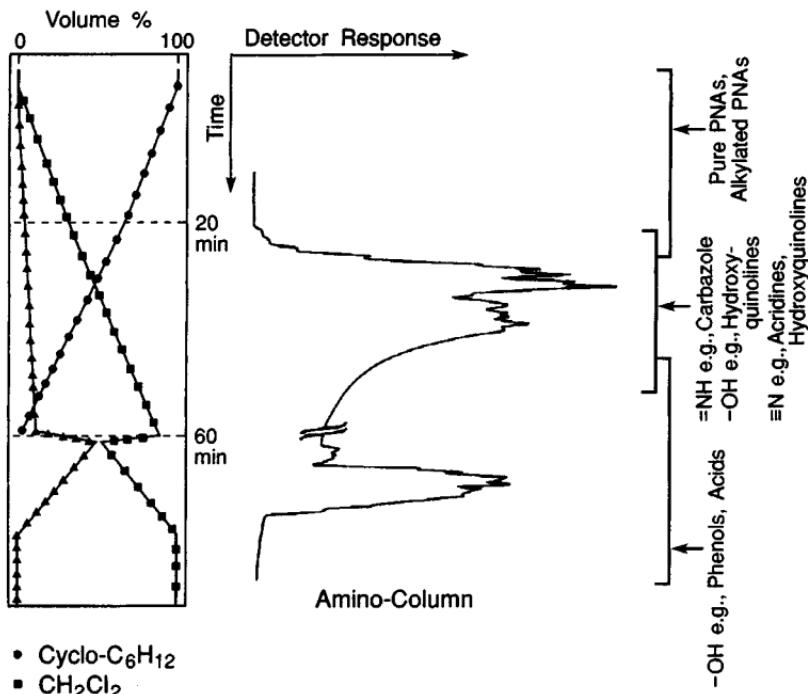


Figure 15.21. HPLC map of an asphaltene fraction.

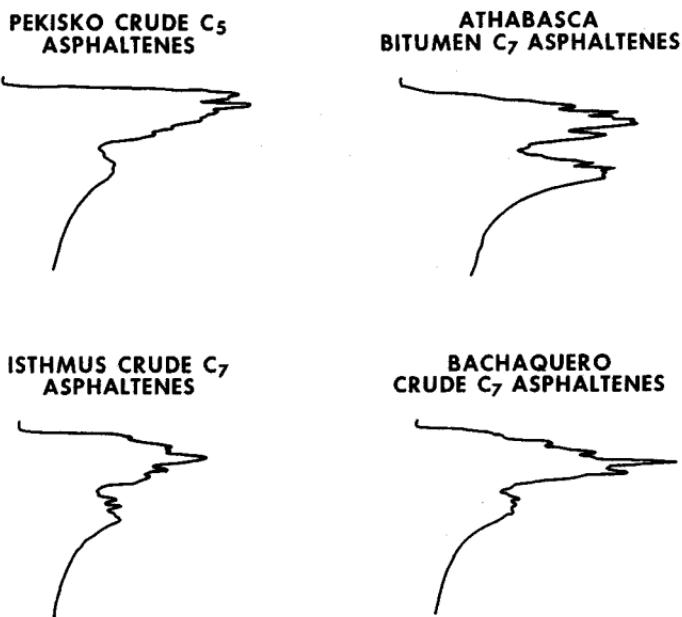


Figure 15.22. HPLC profiles of two different asphaltenes.

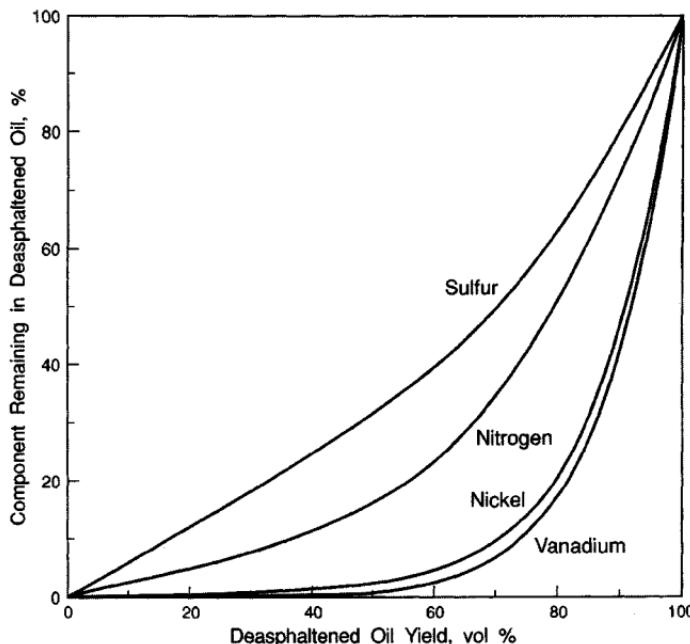


Figure 15.23. Product yields and properties for the deasphalting process.

of the various components such as nitrogen (Chapter 4), metals (Chapter 4), sulfur (Chapter 4), and even coke formers through the carbon residue (Chapter 5) remaining in the deasphalted oil with yield of deasphalted oil (Fig. 15.23). For a specific feedstock under specific conditions, predictability is not only enhanced but virtually assured.

Furthermore, crude oil itself can be viewed as consisting of two continuous distributions, one of molecular weight and the other of molecular type. Using data from molecular weight studies and elemental analyses, the number of nitrogen and sulfur atoms in the aromatic and polar aromatic fractions can also be exhibited. These data show that not only can every molecule in the resins and asphaltenes have more than one sulfur or nitrogen but also that some molecules probably contain both sulfur and nitrogen. As the molecular weight of the aromatic fraction decreases, the sulfur and nitrogen contents of the fractions also decrease.

In contrast to the sulfur-containing molecules, which appear in both the naphthalene aromatics and the polar aromatic fractions, the oxygen compounds present in the heavy fractions of petroleum are normally found in the polar aromatics fraction. This is emphasized by the detailed fractionation of feedstocks in which the four major fractions are subfractionated and the various properties investigated. For example, using the subfraction and carbon residue data illustrates the overlap of the

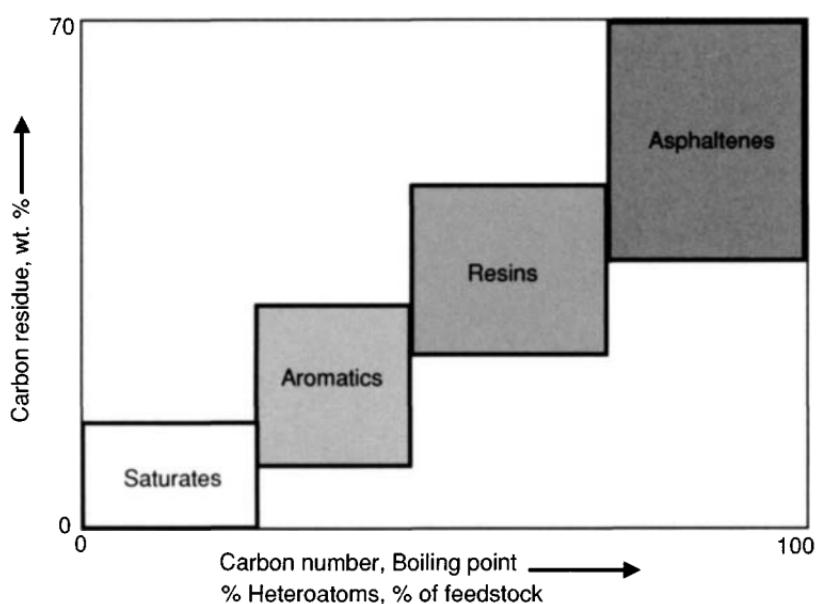


Figure 15.24. Carbon residue data and fraction overlap.

various fractions and enhances the principle that petroleum is indeed a continuum of chemical types (Fig. 15.24).

More recent work (Long and Speight, 1989) involved the development of a different type of compositional map using the molecular weight distribution and the molecular type distribution as coordinates. The separation involved the use of an adsorbent such as clay (Chapter 10) or a gel as used in gel permeation chromatography (Chapter 10), and the fractions were characterized by *solubility parameter* as a measure of the polarity of the molecular types. The molecular weight distribution can be determined by gel permeation chromatography. Using these two distributions, a map of composition can be prepared using molecular weight and solubility parameter as the coordinates for plotting the two distributions. Such a composition map can provide insights into many separation and conversion processes used in petroleum refining.

The molecular type was characterized by the polarity of the molecules, as measured by the increasing adsorption strength on an adsorbent. At the time of the original concept, it was unclear how to characterize the continuum in molecular type or polarity. For this reason, the molecular type coordinate of the first maps was the yield of the molecular types ranked in order of increasing polarity. However, this kind of map can be somewhat misleading because the areas are not related to the amounts of material in a given type. The horizontal distance on the plot is a

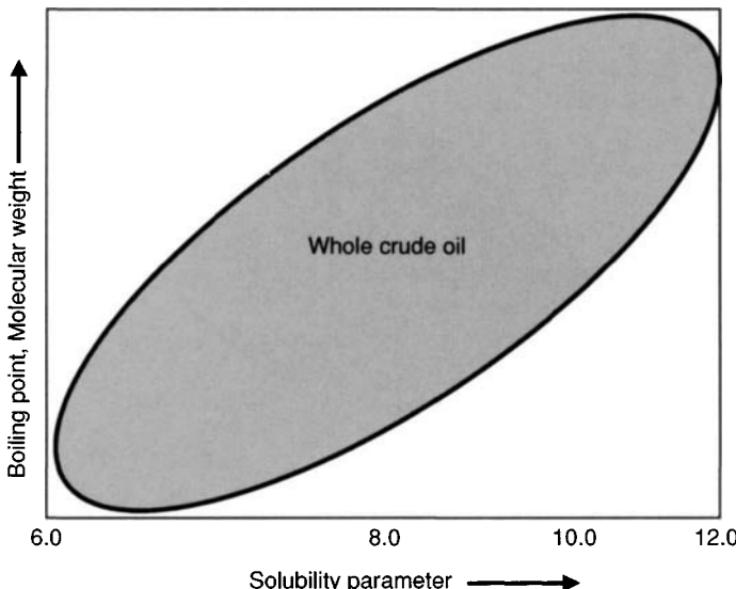


Figure 15.25. Gel permeation chromatography map and solubility parameter.

measure of the yield, and there is not a continuous variation in polarity for the horizontal coordinate. It was suggested that the solubility parameter of the different fractions could be used to characterize both polarity and adsorption strength.

In an attempt to remove some of these potential ambiguities, more recent developments of this concept have focused on the solubility parameter. The simplest map that can be derived using the solubility parameter is produced with the solubility parameters of the solvents used in solvent separation procedures, equating these parameters to the various fractions. However, the solubility parameter boundaries determined by the values for the eluting solvents that remove the fractions from the adsorbent offer a further step in the evolution of petroleum maps (Figs. 15.25 and 15.26) (Long and Speight, 1998).

Measuring the overall solubility parameter of a petroleum fraction is a time-consuming chore. Therefore, it is desirable to have a simpler, less time-consuming measurement that can be made on petroleum fractions that will correlate with the solubility parameter and thus give an alternative continuum in polarity. In fact, the hydrogen-to-carbon atomic ratio and other properties of petroleum fractions that can be correlated with the solubility parameter (e.g., Fig. 15.27) (Wiehe, 1992; Speight, 1994; Wiehe, 1995; Wiehe, 1996) also provide correlation for the behavior of crude oil.

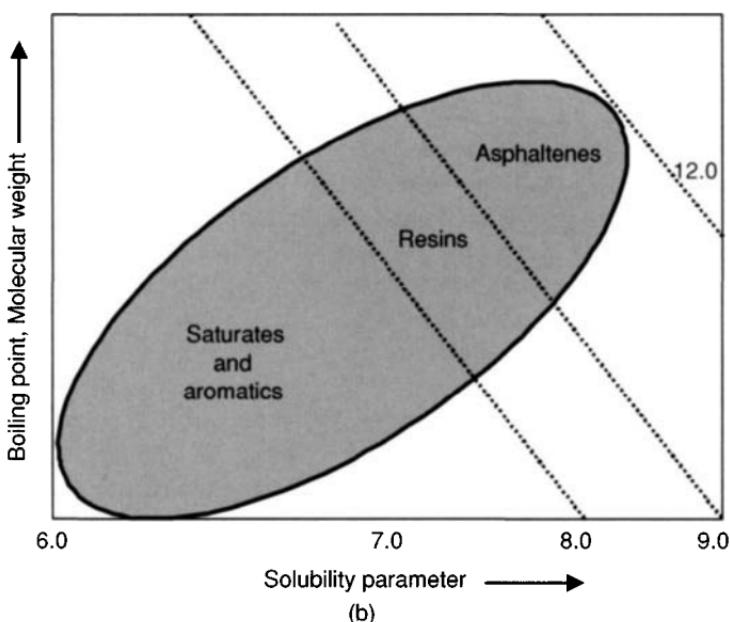
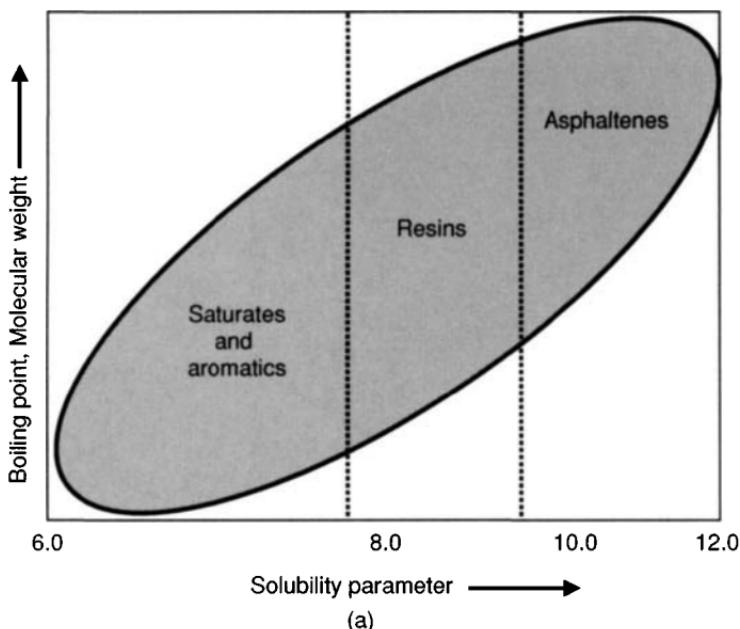


Figure 15.26. Gel permeation chromatography map and solubility parameter profile (a) one dimensional using solubility parameter and (b) two dimensional using solubility parameter and molecular weight.

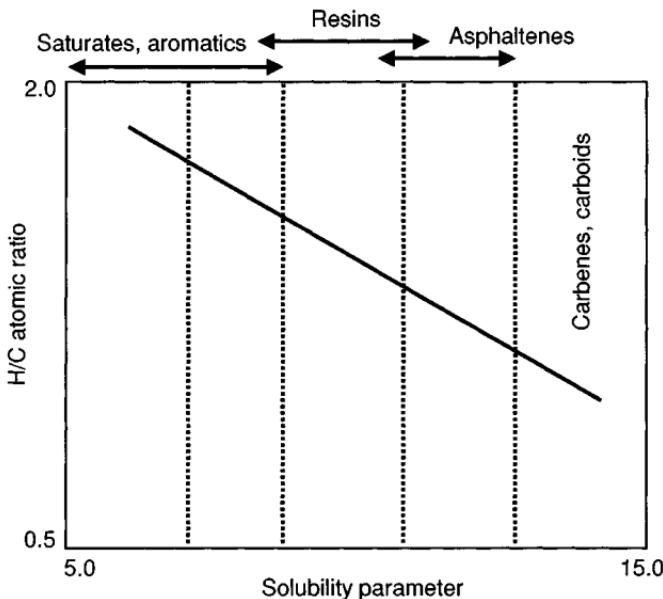


Figure 15.27. Atomic hydrogen-to-carbon ratio and solubility parameter.

15.2.1. Property Predictions

Although there are many maps that can be derived from the fractionation of petroleum, for convenience only selected maps are used here.

A composition map can be used to show where a particular physical or chemical property tends to concentrate on the map. For example, the coke-forming propensity, i.e., the amount of the carbon residue, is shown for various regions on the map for a sample of atmospheric residuum (Fig. 15.28) (Long and Speight, 1998). The plot shows molecular weight plotted against weight percent yield in order of increasing polarity. The dashed line is the envelope of composition of the total sample. The slanted lines show the boundaries of solvent-precipitated fractions, and the vertical lines show the boundaries of the fractions obtained by clay adsorption of the pentane-deasphalted oil.

The boundary for toluene precipitation shows that there are no toluene-insoluble materials in this particular residuum because there is no material of sufficiently high polarity or molecular weight to be insoluble in toluene. If there were, it would have a carbon residue greater than 50. Moving down the right-hand side of the map, the first fraction is the *n*-heptane-insoluble fraction or heptane asphaltenes. The carbon residue (Chapter 5) of this fraction is approximately 48% by weight, which is typical of heptane asphaltenes from a wide variety of crude oils. Moving down

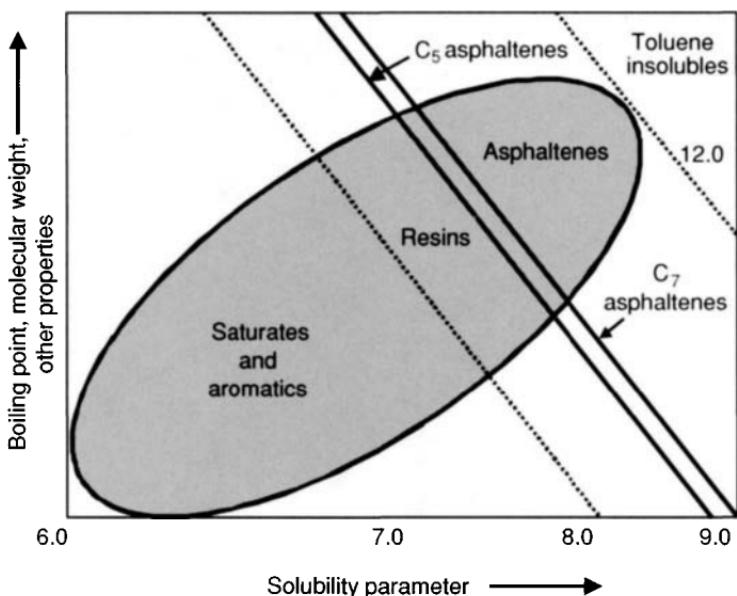


Figure 15.28. Gel permeation chromatography map and property prediction.

to the pentane asphaltene boundary, an insoluble fraction is shown that includes all the heptane asphaltenes as well as lower-molecular-weight polar species and a small amount of high-molecular-weight aromatics. This encompasses an insoluble fraction with a carbon residue of approximately 39% by weight.

The region of the map below the pentane-insoluble boundary corresponds to pentane-deasphalted oil from the original residuum. The saturate, aromatic, and polar fractions were separated by adsorption of the deasphalted oil over clay. The saturates show a zero carbon residue, and the aromatics are only a little higher but still less than 1.0% by weight. The coke-forming constituents in the deasphalted oil are the polar aromatics, which have a carbon residue of approximately 15.0% by weight. The carbon residue balance shown in the inset table shows that almost all of the coke-forming materials (97.6%) are in the asphalt and other lower-molecular-weight polar compounds. This is further evidence of the similarity, with the exception of molecular weight, between asphaltenes and the lower-molecular-weight polar species in deasphalted oil.

15.2.2. Predicting Separations

A composition map can be very useful for predicting the effectiveness of various types of separations processes as applied to petroleum (Fig. 15.29) (Long and Speight, 1998).

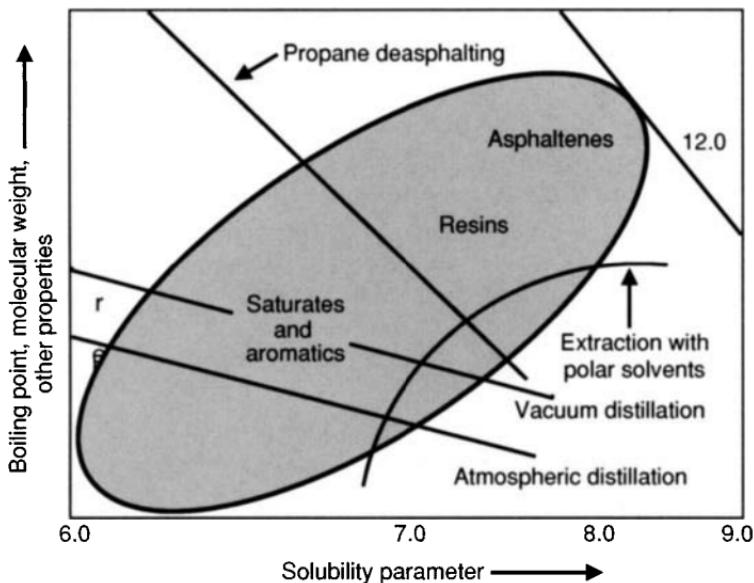


Figure 15.29. Gel permeation chromatography map and prediction of separation processes.

These processes are adsorption, distillation, solvent precipitation with relatively nonpolar solvents, and solvent extraction with polar solvents. The vertical lines show the cut points between saturate aromatics and polar aromatics as determined by clay chromatography. The slanted lines show how distillation, extraction, and solvent precipitation can divide the composition map. The line for distillation divides the map into distillate, which lies below the dividing line, and bottoms, which lies above the line. As the boiling point of the distillate is raised, the line moves upward, including higher-molecular-weight materials and more of the polar species in the distillate and rejecting lower-molecular-weight materials from the bottoms. As more of the polar species are included in the distillate, the carbon residue of the distillate rises.

The solvent precipitation lines and solvent extraction lines are determined by solubility theory, and they move up and down depending on the solvent used, as well as the operating conditions of the separation. For example, with *n*-paraffins as precipitating agents, the cut line is approximately that for *n*-heptane deasphalting. Higher-molecular-weight *n*-paraffins move the cut line up, and lower-molecular-weight *n*-paraffins move it down. Therefore, higher paraffins precipitate high-molecular-weight asphalt and low-molecular-weight paraffins precipitate soft, oily asphalt.

The slope and position of the cut line also depend on the solubility parameter of the precipitating solvent as well as the temperature of operation. For paraffin solvents, the overall solubility parameter of the solvent is to the left of the composition

map and the cut line is the right-hand wing of the solubility bell curve as it cuts through the composition map.

The cut line for extraction with polar solvents such as phenol, cresol, *n*-methyl-pyrrolidone, and furfural is slanted in the opposite direction from solvent precipitation, because the solubility parameter of the polar solvent lies to the right of the composition map. Thus the cut line is the left-hand wing of the solubility bell curve of the polar solvent. It moves up and down and left and right as the solubility parameter of the polar solvent is changed. Furthermore, it is also sensitive to the operating conditions of the extraction, such as temperature and solvent-to-oil ratio.

15.2.3. Process Predictability

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 aromatics to saturates and polar aromatics to either aromatics or saturates (Fig. 15.30) (Long and Speight, 1998). 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

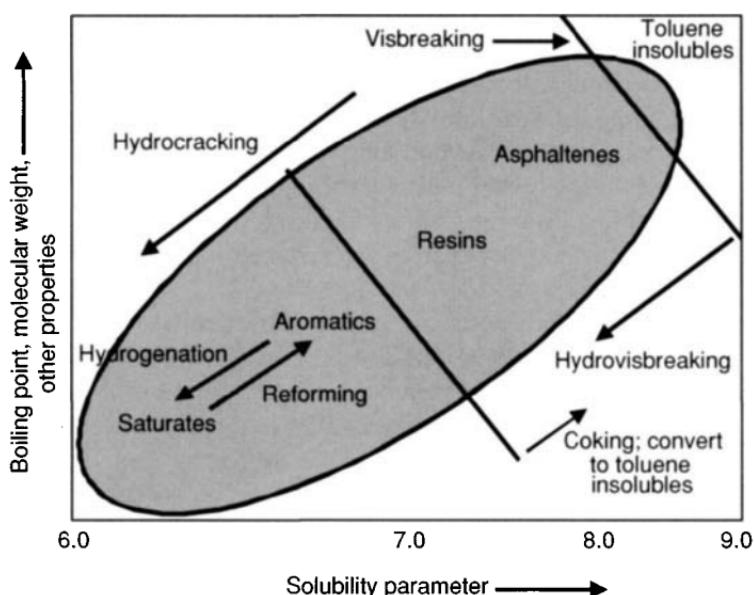


Figure 15.30. Gel permeation chromatography map and thermal processes.

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 method. Thus conversion processes can change the shape and size of the composition map.

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

15.3. EPILOG

The data derived from any one or more of the evaluation techniques described in this text give an indication of the characteristics of the feedstock as well as options for feedstock processing and for the prediction of product properties.

Other properties may also be required for more detailed evaluation of the feedstock and for comparison between feedstocks, even though they may not play any role in dictating which refinery operations are necessary for processing.

However, proceeding from the raw evaluation data to full-scale production is not the preferred step. Further evaluation of feedstock processability is usually through the use of a pilot-scale operation followed by scale-up to a demonstration plant. It will then be possible to develop accurate relationships between the data obtained from the actual plant operations. After that, feedstock mapping can play an important role to assist in the various tweaks that are needed to maintain a healthy process.

Indeed, the use of physical properties for feedstock evaluation has continued in refineries and in process research laboratories to the present 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.

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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 of this book.

ABN separation: a method of fractionation by which petroleum is separated into acidic, basic, and neutral constituents.

Accuracy: the degree of conformity of a measured value to the true value; 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 petroleum oil is treated 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 structure (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^+).

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 $^{\circ}F$, 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.

API gravity: a measure of the *lightness* or *heaviness* of petroleum that is related to density and specific gravity.

$${}^{\circ}\text{API} = (141.5/\text{sp gr } @ 60^{\circ}\text{F}) - 131.5$$

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 hydrocarbons (q.v.) or alicyclic hydrocarbons (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 (naphthalenes).

Asphalt: the nonvolatile product obtained by distillation and treatment of an asphaltic crude oil; a manufactured product.

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.

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).

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 of which the members 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 equivalent boiling point (AEBP): a mathematical method of estimating the boiling point at atmospheric pressure of nonvolatile fractions of petroleum.

Atmospheric residuum: a residuum (q.v.) obtained by distillation of a crude oil under atmospheric pressure that boils above 350°C (660 F).

Attapulgus clay: see Fuller's earth.

Average particle size: the weighted average particle diameter of a catalyst.

Base number: the quantity of acid, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrated 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.

Baumé gravity: the specific gravity of liquids expressed as degrees on the Baumé ($^{\circ}\text{Bé}$) scale; for liquids lighter than water:

$$\text{sp gr } 60^{\circ}\text{F} = 140/(130 + {}^{\circ}\text{Bé})$$

and for liquids heavier than water:

$$\text{sp gr } 60^{\circ}\text{F} = 145/(145 - {}^{\circ}\text{Bé})$$

Bauxite: mineral matter used as a treating agent; hydrated aluminum oxide formed by the chemical weathering of igneous rocks.

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.

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.

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 index: the number of *milligrams* of bromine that will react with 100 g of sample; used mostly for stocks that have an unusually low olefin content.

Bromine number: the number of *grams* of bromine absorbed by 100 g of sample, which indicates the percentage of double bonds in the material.

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 one pound of water one degree Fahrenheit.

Bubble point: the temperature at which incipient vaporization of a liquid in a liquid mixture occurs, corresponding with the equilibrium point of 0 percent vaporization or 100 percent condensation.

Bumping: the knocking against the walls of a still occurring during distillation of petroleum or a petro-

leum 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.

C₁, C₂, C₃, C₄, C₅ 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.

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 inventor 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 temperature (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 ($^{\circ}\text{R} = ^{\circ}\text{F} + 460$), to the specific gravity at $60^{\circ}\text{F}/60^{\circ}\text{F}$:

$$K = (T_B)^{1/3} / \text{sp. gr.}$$

and which ranges from 12.5 for paraffinic stocks to 10.0 for the highly aromatic stocks; also called the Watson characterization factor.

Chelating agents: complex-forming agents having the ability to solubilize heavy metals.

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 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 due to 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 make-up of petroleum.

Composition map: a means of illustrating the chemical make-up of petroleum using chemical and/or physical property data.

Con Carbon: see **Carbon residue.**

Conradson carbon residue: see **Carbon residue.**

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 still: distillation (q.v.) equipment in which crude oil is separated into various products.

Cumene: a colorless liquid [C₆H₅CH(CH₃)₂] used as an aviation gasoline blending component and as an intermediate in the manufacture of chemicals.

Cut point: the boiling temperature division between distillation fractions of petroleum.

Cyclic hydrocarbons: see **Alicyclic hydrocarbons**

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.

Deasphalting: removal of a solid powdery asphaltene fraction from petroleum by the addition of the 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.

Dehydrocyclization: any process by which both dehydrogenation and cyclization reactions occur.

Dehydrogenation: the removal of hydrogen from a chemical compound; for example, the removal of two hydrogen atoms from butane to make butene(s) as well as the removal of

additional hydrogen to produce butadiene.

Delayed coking: a coking process in which the thermal reactions are allowed to proceed to completion 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 cycle: a repeated succession of operations representing the idealized working behavior of the fluids in a diesel engine.

Diesel fuel: fuel used for internal combustion in diesel engines; usually the fraction that distills after kerosene.

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.).

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

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 percent 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 refers to 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.

Effective viscosity: see **Apparent viscosity**.

Engler distillation: a standard test for determining the volatility characteristics of a gasoline by measuring the percent distilled at various specified temperatures.

Ethanol: see Ethyl 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 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: term for a substance that will burn readily.

Flammable liquid: a liquid having 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.

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 and 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 the constituent fractions using solvent or adsorbent methods; chemical agents such as sulfuric acid may also be used.

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 a 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.

Grain alcohol: see **Ethyl alcohol**.

Gum: an insoluble, tacky, semisolid material formed as a result of the storage instability and/or the thermal instability of petroleum and petroleum products.

Heavy ends: the highest boiling portion of a petroleum fraction; see also **Light ends**.

Heavy oil: petroleum having an API gravity of less than 20°.

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 resource: resources such as petroleum and natural gas that can produce naturally occurring hydrocarbons without the application of conversion processes.

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.

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 to 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: term for two or more fluids that do not have complete mutual solubility and coexist as separate phases.

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 (compacted) and tested as a unit.

Individuals: conceivable constituent parts of the population.

Initial boiling point: the recorded temperature 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.

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.

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 having 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 having an API gravity greater than 20°.

Ligroine (Ligroin): a saturated petroleum naphtha boiling in the range of 20 to 135°C (68 to 275°F) and suitable for general use as a solvent; also called **benzine** or **petroleum ether**.

Liquefied petroleum gas: propane, butane, or mixtures thereof, gaseous at atmospheric temperature and pressure, held in the liquid state by pressure to facilitate storage, transport, and handling.

Lot: a quantity of bulk material of similar composition whose properties are under study.

Lube: see **Lubricating oil**.

Lubricating oil: a fluid lubricant used to reduce friction between bearing surfaces.

Maltenes: that fraction of petroleum that is soluble in, for example, pentane or heptane; deasphalted 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 having a soft, mayonnaise-like consistency; not recommended as a food additive!

MEK: methyl ethyl ketone.

Mercaptans: organic compounds having the general formula R-SH.

Methanol: see Methyl alcohol.

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 using 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.

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 or nafta: pre-Common Era (Greek) term for naphtha (q.v.).

Naphtha: a generic term applied to refined, partly refined, or unrefined petroleum products and liquid products of natural gas, the majority of which distills 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; also, there are also those 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: term for a fluid that exhibits a change of viscosity with flow rate.

Octane number: a number indicating the antiknock characteristics of gasoline.

Oils (fraction): that 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: that 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 that 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.

Peri-condensed 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.

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 **Porphyrins**.

pH adjustment: neutralization.

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.

Pitch: the nonvolatile, brown to black, semisolid to solid viscous product from the destructive distillation of many bituminous or other organic materials, especially coal.

PNA: a polynuclear aromatic compound (q.v.).

PONA analysis: a method of analysis for paraffins (P), olefins (O), naphthenes (N), and aromatics (A).

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.

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 degree to which a measurement can be repeated

Primary structure: the chemical sequence of atoms in a molecule.

Propane asphalt: see **Solvent asphalt.**

Propane deasphalting: solvent deasphalting using propane as the solvent.

Pyrobitumen: see **Asphaltoid.**

Pyrolysis: exposure of a feedstock to

high temperatures in an oxygen-poor environment.

Pyrophoric: term for 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: that 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.

Reduction: 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 are generated.

Reid vapor pressure: a measure of the volatility of liquid fuels, especially gasoline.

Repeatability: the difference between two individual test results reported by a single analyst on two test portions of the same material 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 (reference: ASTM C670).

Reproducibility: The difference between two individual test results reported by two laboratories on two test portions of the same material 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.

Residual asphalt: see Straight-run asphalt.

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.

Resins: that 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.

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 demarcated 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.

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.

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 (q.v.) or by light hydro-

carbon (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**.

Specific gravity: the mass (or weight) of a unit volume of any substance at a specified temperature compared to 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, q.v.); the production of a product that, to 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 which 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.

Strata: segments of a lot that may vary with respect to the property under study.

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: see **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 non-catalytic 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: term that 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); that portion of petroleum that boils above a selected temperature such as 510°C (950°F) or 565°C (1050°F).

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 m² 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:

$$a = \frac{10\text{sg} - 1.0752 \log (\text{SUV} - 38)}{10\text{sg} - \log (\text{SUV} - 38)}$$

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 index-: see **VI**.

Watson characterization factor: see **Characterization factor**.

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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