

ANALYTICAL METHODS AND TECHNIQUES APPLIED TO CRUDE OIL AND PETROLEUM PRODUCTS

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Summary

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.

Knowledge of the composition of petroleum allows the refiner to optimize the conversion of raw petroleum into high value products. Also, knowledge of the molecular composition of petroleum allows the environmentalist to consider the biological impact of environmental exposure. 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). Having decided what characteristics are necessary, it then remains to describe the product in terms of a specification. This entails selecting suitable test methods and setting appropriate limits.

Many specifications in widespread use have evolved usually by the addition of extra clauses (rarely is a clause deleted). This has resulted in unnecessary restrictions that, in turn, result in increased cost of the products specified.

1. Petroleum Analysis

1.1. Introduction

Petroleum (also called *crude oil*) (ASTM Test Method D4175) meaning literally *rock oil* is the term used to describe a myriad of hydrocarbon-rich fluids that has accumulated in subterranean reservoirs and which vary dramatically in properties (Table 1). The terminology and definitions applied to petroleum have been defined elsewhere in this work (Section 6.186) and will not be repeated here. 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 (Speight, 2001, 2002) 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. 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 oil. Sulfur content, another crucial and primary property of a crude oil, is also readily determined. Certain composite characterization values, calculated from density and midboiling-point correlate better with molecular composition than density alone.

Crude oil	Specific gravity	API gravity
US Domestic		
California	0.858	33.4
Oklahoma	0.816	41.9
Pennsylvania	0.800	45.4
Texas	0.827	39.6
Texas	0.864	32.3
Foreign		
Bahrain	0.861	32.8
Iran	0.836	37.8
Iraq	0.844	36.2
Kuwait	0.860	33.0

Saudi Arabia	0.840	37.0
Venezuela	0.950	17.4

Table 1. Variation in crude oil properties with location.

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.

Crude oil is sold in the form of gasoline, solvents, diesel and jet fuel, heating oil, lubricant oils and asphalts or it is converted to petrochemical feedstocks such as ethylene, propylene, the butenes, butadiene, and isoprene. These feedstocks are important, for 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 molecules into these products. Conversion processes include coking, hydrocracking, and catalytic cracking to break large molecules into smaller fractions; hydrotreating to reduce heteroatoms and aromatics creating environmentally acceptable products; 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 exposure. Molecular composition is needed not only to identify the sources of contamination but also to understand the fate and effects of its potentially hazardous components.

In addition, knowledge of the composition of petroleum allows the 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).

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 are extremely important. But product characteristics and specifications are also important.

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

by the addition of extra clauses (rarely is a clause deleted). This has resulted in unnecessary restrictions that, in turn, result in increased cost of the products specified.

1.2. History

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. In addition, an analytical distillation of petroleum was carried out in the early 1870's. Further developments of the analytical chemistry of petroleum continued throughout the century.

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 since 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 designing new methods as well as 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 analysis, 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' 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 upon 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.

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 had qualitative importance. This led to the development of a systematic basis for group separations but it was not until the present century that procedures became highly standardized. The American Society for Testing and Materials (ASTM) became active in developing standard tests for petroleum and petroleum products in 1904 from which evolved with the Technical Committee D2 on Petroleum Products and Lubricants with a scope that included almost all petroleum products. Hence the designation of many standards for the evaluation of petroleum and petroleum products as *ASTM D* standards.

These developments, taken 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. During this time, the determination of functional groups, such as carboxyl, ester, tin-saturated 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, since 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 be titrated accurately by use of the correct indicator. A similar approach could be used with esters, where a carboxyl group is formed upon 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.

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 employed 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, 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. Counter-current solvent extraction has also been employed 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 employed 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.

In summary, the nineteenth and twentieth centuries were periods 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.

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Biographical Sketch

Dr. James G. Speight has a Ph.D. in Organic Chemistry from the University of Manchester, England, and works for CDW Inc. as an Author/Lecturer/Technical and Business Advisor. Previously, he was Chief Executive Officer at the Western Research Institute (1990–1998). Dr. Speight has thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research in defining the use of chemistry of heavy oil and coal. He has well over three hundred publications, reports, and presentations detailing these research activities. Dr. Speight is currently editor of the journal *Petroleum Science and Technology* (formerly *Fuel Science and Technology International*), editor of the journal *Energy Sources*, and co-editor of the journal *Reviews in Process Chemistry and Engineering*. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemistry and Adjunct Professor of Chemical Engineering at the University of Wyoming as well as Adjunct Professor of Chemical and Fuels Engineering at the University of Utah. Dr. Speight is the author/editor/compiler of nineteen books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, For Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996. Dr. Speight also received the degree of

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