PETROLEUM: CHEMISTRY, REFINING, FUELS AND PETROCHEMICALS- BASICS

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Summary

Petroleum and the equivalent term crude oil, cover a wide assortment of materials consisting of mixtures of hydrocarbons and other compounds containing variable amounts of sulfur, nitrogen, and oxygen, which may vary widely in volatility, specific gravity, and viscosity. Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks. Because petroleum is a mixture of widely varying constituents and proportions, its physical properties also vary widely and the color from colorless to black and there is the consistent use of archaic names. Thus, confusion about the petroleum nomenclature still exists.

It is the purpose of this section to provide some semblance of order into the disordered state that exists in petroleum terminology. Definitions are presented for petroleum and related materials using the following categories: (1) materials of natural origin, (2) manufactured materials, and (3) materials that are integral fractions derived from the

natural or manufactured products. In addition definitions of petroleum constituents, petroleum products, heavy oil, tar sand bitumen and other naturally occurring carbonaceous species are also given.

Information about the composition and standard test methods for determining the properties of petroleum, as well as methods for determining both, are also included.

1. Definitions and Terminology

Petroleum is a naturally occurring mixture of hydrocarbons, generally in a liquid state, which may also include compounds of sulfur nitrogen oxygen metals and other elements (ASTM, 2007). The hydrocarbon content may be as high as 97% w/w, for example in the lighter paraffinic crude oil or as low as 50% w/w in heavy crude oil. Petroleum is not a uniform material. In fact, the chemical and physical (fractional) composition of petroleum can vary not only with the location and age of the oil field but also with the depth of the individual well. Indeed, two adjacent wells may produce petroleum with markedly different characteristics.

In the crude state petroleum has minimal value, but when refined it provides high-value liquid fuels, solvents, lubricants, and many other products. 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.

Since there is a wide variation in the properties of crude petroleum (Table 1), the proportions in which the different constituents occur vary with origin. Some crude oils have higher proportions of the lower boiling components and other naturally occurring materials (such as heavy oil and bitumen) have higher proportions of higher boiling components (asphalt constituents and residuum).

Petroleum		**Specific**		**API**		**Residuum**
		gravity		gravity		>1000 F
						% v/v
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

Table 1: Typical variations in the properties of petroleum.

For the purposes of terminology, it is preferable to subdivide petroleum and related materials into three major classes (Table 2: (1) materials of natural origin, (2) manufactured materials, and (3) materials that are integral fractions derived from the natural or manufactured products.

Natural		**Derived**		**Manufactured**	
materials		materials		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				Tar	
Coal				Pitch	
*Bitumen from tar sand deposits.					
**Usually thermal products from petroleum processing.					

Table 2 Sub-division of petroleum and similar materials into various sub-groups.

1.1. Native Materials

1.1.1. Petroleum

Petroleum and the equivalent term *crude oil*, cover a wide assortment of materials consisting of mixtures of hydrocarbons and other compounds containing variable amounts of sulfur, nitrogen, and oxygen, which may vary widely in volatility, specific gravity, and viscosity. Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks (Speight, 2007). Because petroleum is a mixture of widely varying constituents and proportions, its physical properties also vary widely and the color from colorless to black.

Petroleum occurs underground, at various pressures depending on the depth. Because of the pressure, it contains considerable natural gas in solution. Petroleum underground is much more fluid than it is on the surface and is generally mobile under reservoir conditions because the elevated temperatures (the *geothermal gradient*) in subterranean formations decrease the viscosity. Although the geothermal gradient varies from place to place, it is generally on the order of 25 to 30^{o}C/km (15^{o}F/1000 ft or 120^{o}C/1000 ft, i.e. 0.015^{o}C per foot of depth or 0.012^{o}C per foot of depth).

The major components of petroleum are *hydrocarbons*, compounds of hydrogen and carbon that display great variation in their molecular structure. The simplest hydrocarbons are a large group of chain-shaped molecules known as the *paraffins*. This broad series extends from methane, which forms natural gas, through liquids that are refined into gasoline, to crystalline waxes. A series of ring-shaped hydrocarbons, known as the *naphthenes*, ranges from volatile liquids such as *naphtha* to high molecular weight substances isolated as the *asphaltene* fraction. Another group of ring-shaped hydrocarbons is known as the *aromatics*; the chief compound in this series is benzene, a popular raw material for making petrochemicals.

Non-hydrocarbon constituents of petroleum include organic derivatives of nitrogen, oxygen, sulfur, and the metals nickel and vanadium. Most of these impurities are removed during refining.

1.1.2. Heavy Oil

Heavy crude oil is a type of crude oil which does not flow easily. It is a relative term, compared to (conventional) light crude oil, but relates to technical issues involved in production, transportation, and refining. The physical properties that distinguish heavy oil from conventional oil include higher viscosity and specific gravity, as well as molecular composition.

The definition of heavy oil is usually based on the API gravity or viscosity, and the definition is quite arbitrary although there have been attempts to rationalize the definition based upon viscosity, API gravity, and density. For example, heavy oils were considered to be those crude oils that had gravity somewhat less than 20^{o} API with the heavy oils falling into the API gravity range 10 to 15^{o}. For example, Cold Lake heavy crude oil has an API gravity equal to 12^{o} and extra heavy oils, such as tar sand bitumen, usually have an API gravity in the range 5 to 10^{o} (Athabasca bitumen: 8^{o}API). Residua would vary depending upon the temperature at which distillation was terminated but usually vacuum residua are in the range 2 to 8^{o} API (Speight and Ozum, 2002; Speight, 2007).

1.1.3. Bitumen

Bitumen is a naturally-occurring material that is found in deposits where the permeability is low and passage of fluids through the deposit can only be achieved by prior application of fracturing techniques (Abraham, 1945; Hoiberg, 1964).

The expression *tar sand* is commonly used in the petroleum industry to describe sandstone reservoirs that are impregnated with a heavy, viscous bituminous material.

Alternative names, such as *bituminous sand* or *oil sand*, are gradually finding usage, with the former name (bituminous sands) more technically correct. The term *oil sand* is also used in the same way as the term *tar sand*, and these terms are used interchangeably.

Tar sands have been defined in the United States (FE-76-4) 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, oil sands, and rock asphalt.*

The recovery of the bitumen from tar sand formations depends to a large degree on the composition and construction of the sands. Generally, the bitumen found in tar sand deposits is an extremely viscous material that is *immobile under reservoir conditions* and cannot be recovered through a well by the application of secondary or enhanced recovery techniques. In fact, the bitumen in tar sand formations requires a high degree of thermal stimulation for recovery to the extent that some thermal decomposition may have to be induced. Current recovery operations of bitumen in tar sand formations involve use of a mining technique.

In many countries other than North America, the term bitumen is applied not only to any of various solid or semisolid mixtures of hydrocarbonaceous materials that occur in nature bit also to the refinery products which are obtained as residues from the distillation of petroleum (Speight, 1999). In Great Britain and continental Europe the terms *bitumen* and *asphaltic bitumen* are employed only with reference to the black or brown petroleum-like substances that are called *asphalt* in the United States.

1.1.4. Wax

Naturally occurring wax, often referred to as *mineral wax*, occurs as a yellow to dark brown, solid substance that is composed largely of paraffins. Fusion points vary from 60°C (140°F) to as high as 95°C (203°F). They are usually found associated with considerable mineral matter, as a filling in veins and fissures or as an interstitial material in porous rocks. The similarity in character of these native products is substantiated by the fact that, with minor exceptions where local names have prevailed, the original term *ozokerite* (*ozocerite*) has served without notable ambiguity for mineral wax deposits.

Ozokerite (*ozocerite*), from the Greek meaning *odoriferous wax*, is a naturally occurring hydrocarbon material composed chiefly of solid paraffins and cycloparaffins (i.e. hydrocarbons). Ozocerite usually occurs as stringers and veins that fill rock fractures in tectonically disturbed areas. It is predominantly paraffinic material (containing up to 90 percent non-aromatic hydrocarbons) with a high content (40 to 50 percent) of normal or slightly branched paraffins as well as cyclic paraffin derivatives. Ozocerite contains approximately 85% carbon, 14% hydrogen, and 0.3% each of sulfur and nitrogen and is, therefore, predominantly a mixture of pure hydrocarbons; any non-hydrocarbon constituents are in the minority. Ozocerite is soluble in solvents that are commonly employed for dissolution of petroleum derivatives, e.g. toluene, benzene, carbon disulfide, chloroform, and ethyl ether.

On distillation in a current of superheated steam, ozokerite yields a candle-making material resembling the paraffin wax obtained from petroleum, but of higher melting-point, and therefore of greater value if the candles made from it are to be used in hot climates. There are also obtained in the distillation light oils and a product resembling vaseline. The residue in the stills consists of a hard, black, waxy substance, which in admixture with rubber is employed under the name of okonite as an electrical insulator. Mining of ozokerite has diminished due to competition from paraffin was manufactured from petroleum. Ozocerite has a higher melting range than most petroleum waxes and is still favored for some applications, such as electrical insulators, candles, or as the filling in extra-soft paper tissues.

1.1.5. Asphaltite

Asphaltites are a variety of naturally occurring, dark brown to black, solid, nonvolatile bituminous substances that are differentiated from *bitumen* primarily by their high content of material insoluble in the common organic solvents and high yields of thermal coke. The resultant high temperature of fusion (approximate range 115 to 330°C, 240 to 625°F) is characteristic. The names applied to the two rather distinct types included in this group are now accepted and used for the most part without ambiguity.

Gilsonite was originally known as *uintaite* from its discovery in the Uinta Basin of western Colorado and eastern Utah. It is characterized by a bright luster and a carbon residue in the range 10 to 20% by weight. The mineral occurs in nearly vertical veins varying from about an inch to many feet in width and is relatively free of occluded inorganic matter. Samples taken from different veins and across the larger veins may vary somewhat in softening point, solubility characteristics, sulfur content, and so on, but the variation is not great. It is evident in all instances that it is essentially the same material, and it is therefore appropriate to apply a single name to this mineral. However, caution should be exercised in using the same term without qualification for similar materials until it can be shown that they are equivalent to *gilsonite*.

The second recognized type in this category is *grahamite*, which is very much like Gilsonite in external characteristics but is distinguished from the latter by its black streak, relatively high fixed carbon value (35 to 55%), and high temperature of fusion, which is accompanied by a characteristic intumescence. The undifferentiated term *grahamite* must be used with caution; similarities in the characteristics of samples from different areas do not necessarily imply any chemical or genetic relationship.

A third but rather broad category of asphaltite includes a group of bituminous materials known as *glance pitch*, which physically resemble Gilsonite but have some of the properties of *Grahamite*. They have been referred to as intermediates between the two, but the possibility does exist that they are basically different from *gilsonite* and may represent something between *bitumen* and *grahamite*.

1.1.6. Asphaltoid

Asphaltoids are a further group of brown to black, solid bituminous materials of which the members are differentiated from the *asphaltites* by their infusibility and low solubility in carbon disulfide. These substances have also been designated *asphaltic pyrobitumen*, as they decompose on heating into bitumen-like materials. However, the term *pyrobitumen* does not convey the impression intended; thus the members of this class are referred to as *asphaltoids* since they closely resemble the asphaltites.

Pyrobitumen, is a naturally occurring solid organic substance that is distinguishable from bitumen (*q.v.*) by being infusible and insoluble. When heated, however, pyrobitumen generates, or transform into, bitumen-like liquid and gaseous hydrocarbon compounds. Pyrobitumen may be either asphaltic or non-asphaltic. The asphaltic pyrobitumen are derived from petroleum, are relatively hard, and have a specific gravity below 1.25. They do not melt when heated but swell and decompose (*intumesce*).

1.1.7. Bituminous Rock and Bituminous Sand

Bituminous rock and *bituminous sand* (see also *bitumen*) are those formations in which the bituminous material is found as a filling in veins and fissures in fractured rocks or impregnating relatively shallow sand, sandstone, and limestone strata. The deposits contain as much as 20% bituminous material, and if the organic material in the rock matrix is bitumen, it is usual (although chemically incorrect) to refer to the deposit as *rock asphalt* to distinguish it from bitumen that is relatively mineral free. A standard test (ASTM, 2007) is available for determining the bitumen content of various mixtures with inorganic materials, although the use of word *bitumen* as applied in this test might be questioned and it might be more appropriate to use the term *organic residues* to include *tar* and *pitch*

Bituminous rocks generally have a coarse, porous structure, with the bituminous material in the voids. A much more common situation is that in which the organic material is present as an inherent part of the rock composition insofar as it is a diagenetic residue of the organic material detritus that was deposited with the sediment. The organic components of such rocks are usually refractory and are only slightly affected by most organic solvents.

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Biographical Sketch

Dr. Speight has more than 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 and development in refining heavy oil and coal, and related environmental issues. He has well over four hundred publications, reports, and presentations detailing these research activities and has taught more than forty related courses.

Dr. Speight is currently editor of the journal Petroleum Science and Technology (formerly Fuel Science and Technology International) and editor of the journal Energy Sources. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemical and Fuels Engineering at the University of Utah.

Dr. Speight is the author/editor/compiler of more than twenty 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 for his Contributions to Coal Research. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia For Exceptional Work in Petroleum Science in 1997. In 2001, Dr. Speight was also awarded the Einstein Medal of the Russian Academy of Sciences (Natural) in recognition of Outstanding Contributions and Service in the field of Geologic Sciences.