

PROPERTIES AND CLASSIFICATION OF PETROLEUM

PCM 202

PHYSICAL CHEMICAL PROPERTIES OF PETROLEUM

INTRODUCTION

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

PHYSICAL PROPERTIES

ELEMENTAL (ULTIMATE) ANALYSIS

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. It is also of value to determine the amounts of trace elements, such as vanadium, nickel and other metals, in a feedstock since these materials can have serious deleterious effects on catalyst performance during refining by catalytic processes. However, it has 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.

The ultimate analysis (elemental composition) of petroleum is not reported to the same extent as for coal (Speight, 1994). Nevertheless, there are ASTM procedures for the ultimate analysis of petroleum and petroleum products but many such methods may have been designed for other materials. For example, carbon content can be determined by the method designated for coal and coke (ASTM D3178) or by the method designated for municipal solid waste (ASTM E777). There are also methods designated for:

1. Hydro gen content (ASTM D1018, ASTM D3178, ASTM D3343, ASTM D3701, and ASTM E777)
2. Nit rogen conten t (ASTM D3179, ASTM D3228, ASTM D3431, ASTM E148, ASTM E258, and ASTM E778)
3. Oxygen conten t (ASTM E385)
4. Sul fur conten t (ASTM D124, ASTM D1266, ASTM D1552, ASTM D1757, ASTM D2662, ASTM D3177, ASTM D4045 and ASTM D4294).

Of the data that are available, the proportions of the elements in petroleum vary only slightly over narrow limits:

Carbon 83.0 to 87.0%

Hydrogen 10.0 to 14.0%

Nitrogen 0.1 to 2.0%

Oxygen 0.05 to 1.5%

Sulfur 0.05 to 6.0%

Metals (Ni and V) <1000 ppm.

DENSITY AND SPECIFIC GRAVITY

The density and specific gravity of crude oil (ASTM D70, ASTM D71, ASTM D287, ASTM D941, ASTM D1217, ASTM D1298, ASTM D1480, ASTM D1481, ASTM D1555, ASTM D1657, ASTM D4052, 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 and quality of crude oil. Density is 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). Specific gravity is the ratio of the mass of a volume of the 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 48C (398F), the specific gravity is equal to the density in the centimeter–gram–second (cgs) system, since 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=608F (15.6=15.68C). 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. Although density and specific gravity are used extensively, the (American Petroleum Institute) API gravity is the preferred property. This property was derived from the Baume' scale:

$$\text{Degrees Baume} : (140/\text{sp gr}_{60/60^{\circ}\text{F}}) - 130$$

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

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

The specific gravity of petroleum usually ranges from about 0.8 (45.38 API) for the lighter crude oils to over 1.0 (less than 108 API) for heavy crude oil and bitumen. Specific gravity is influenced by the chemical composition of petroleum, but quantitative correlation is difficult to establish. Nevertheless, it is generally recognized that increased amounts of aromatic compounds result in an increase in density, whereas an increase in saturated compounds results in a decrease in density.

Density, specific gravity, or API gravity may be measured by means of a hydrometer (ASTM D287, ASTM D1298, ASTM D1657, IP 160), a pycnometer (ASTM D70, ASTM D941, ASTM D1217, ASTM D1480, and ASTM D1481), by the displacement method (ASTM D712), or by means of a digital density meter (ASTM D4052, IP 365) and a digital density analyzer (ASTM D5002). The pycnometer method (ASTM D70, ASTM D941, ASTM D1217, ASTM D1480, ASTM D1481) for determining density is reliable, precise and requires relatively small test samples. However, because of the time required, other methods such using the hydrometer (ASTM D1298), the density meter (ASTM D4052), and the digital density analyzer (ASTM D5002) 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 D70, ASTM D941, ASTM D1217, ASTM D1480, and ASTM D1481) 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 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, one per cent by weight solids in the sample can raise the density by 0.007 g/cm^3 . The densimeter method (ASTM D4052) 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 which allow conversion of the natural frequency of vibration to sample density. The variation of density with temperature, effectively the coefficient of expansion, is a property of great technical importance, since 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 D1555) are based on an assumption that the coefficient of expansion of all petroleum products is a function (at fixed temperatures) of density alone. Recent work has focused on the calculation and predictability of density using new mathematical relationships.

VISCOSITY

Viscosity is the force in dynes required to move a plane of 1 cm^2 area at a distance of 1 cm from another plane of 1 cm^2 area through a distance of 1 cm in 1 sec. In the cgs system, the unit of viscosity is the poise or centipoise (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 stoke (cm^2/sec), although centistokes (0.01 cSt) is in more common usage; fluidity is simply the reciprocal of viscosity. The viscosity (ASTM D445, D88, D2161, D341, and D2270) 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. Many types of instruments have been proposed for the determination of viscosity. The simplest and most widely used are capillary types (ASTM D445), and the viscosity is derived from the equation:

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

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 m 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.

Various studies have also been made on the effect of temperature on viscosity since the viscosity of petroleum, or a petroleum product, decreases as the temperature increases. 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:

$$\text{Log log } (n+c) = A + B \text{ log } T$$

Where n 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 with a viscosity over 1.5 cSt; it increases only slightly at lower viscosity (0.75 at 0.5 cSt). 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 D2270) was derived. It is established that naphthenic oils have higher viscosity–temperature coefficients than the 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 that 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 998C (2108F), and U is that of the unknown, all at 388C (1008F).

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 tension of petroleum and petroleum products has been studied for many years. The narrow range of values (approximately 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) has rendered the surface tension of little value for any attempted characterization. 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.

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

METALS CONTENT

Heteroatoms (nitrogen, oxygen, sulfur, and metals) are found in every crude oil and the concentrations have to 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 (NOx) and sulfur oxides (SOx) form, respectively. In addition, metals affect many upgrading processes adversely, poisoning catalysts in refining and causing deposits in combustion.

Heteroatoms do 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 to nitrogen. Metals cause particular problems because they poison catalysts used for sulfur and nitrogen removal as well as other processes such as catalytic cracking.

A variety of tests (ASTM D1026, D1262, D1318, D1368, D1548, D1549, D2547 D2599, D2788, D3340, D3341, and D3605) have been designated for the determination of metals on petroleum products. 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. The ash can then be digested with an acid and the solution examined for metal species by atomic absorption (AA) spectroscopy or by inductively coupled argon plasma (ICP) spectrometry. Heavy oils and residua contain relatively high proportions of metals either in the form of salts or as organometallic constituents (such as the metallo-porphyrins), 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, and 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.

THERMAL PROPERTIES

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 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 D2715). A test (ASTM D6) also exists for determining the loss of material when crude oil and asphaltic compounds are heated. Another test (ASTM D20) is a method for the distillation of road tars that might also be applied for estimating the volatility of high molecular weight residues. For some purposes, it is necessary to have information on the initial stage of vaporization. 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 if small quantities of high-boiling components are present. For such purposes, 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 D56, D92, and D93). 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 D92). From the viewpoint of safety, information about the flash point is of most significance at or slightly above the maximum temperatures (308C to 608C, 868F to 1408F) 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 408C (1048F), special precautions are necessary for safe handling. Flash points above 608C (1408F) 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 D323). 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 atm (14.7 psi, absolute) is designated as the boiling point of the liquid.

In each homologous series of hydrocarbons, the boiling points increase with molecular weight, and structure also has a marked influence since it is a general rule that branched paraffin isomers have lower boiling points than the corresponding n-alkane. 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. This particularly applies to alkyl aromatic compounds where alkyl-substituted aromatic compounds can have higher boiling points than polycondensed aromatic systems.

CARBON RESIDUE

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 procedure. The carbon residue is a property that can be correlated with several other properties of petroleum (Speight, 2000); 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.

There are two older methods for determining the carbon residue of a petroleum or petroleum product: the Conradson method (ASTM D189) and the Ramsbottom method (ASTM D524). Both are applicable to the relatively nonvolatile portion of petroleum and petroleum products, which partially decompose when distilled at a pressure of 1 atmosphere. However, crude oil that contains ash-forming constituents will have an erroneously high carbon residue by either method, unless the ash is first removed from the oil; the degree of error is proportional to the amount of ash. A third method, involving micropyrolysis of the sample, is also available as a standard test method (ASTM D4530). The method requires smaller sample amounts 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.

ANILINE POINT

The aniline point of a liquid was originally defined as the consolute or critical solution temperature of the two liquids, 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.

Although it is an arbitrary index (ASTM D611), the aniline point is of 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.

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 D2766). 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:

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

C is the specific heat at $t^{\circ}\text{F}$ of an oil whose specific gravity $60/60^{\circ}\text{F}$ is d ; thus, specific heat increases with temperature and decreases with specific gravity.

ENTHALPY OR HEAT CONTENT

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

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