



5 Physical Properties

5.1 Specific gravity and Density

Specific gravity of liquid (sp. gr.): is defined as the ratio of the density of the liquid to the density of water, both taken at the same temperature and pressure.

$$\text{sp. gr. of liquid} = \frac{\rho_o}{\rho_w}$$

Where ρ_o is the density of liquid

ρ_w is the density of distilled water

Density is the mass of a unit volume of material at a specified temperature and has the dimensions of grams per cubic centimeter (gm/cm³).

Specific gravity is given as sp. gr. 60°/60°F for crude oil and petroleum products, which means that the densities of both the petroleum and the water were measured at 60°F and atmospheric pressure.

$$\text{sp. gr. of oil at } 60^\circ/60^\circ\text{F} = \frac{\rho_o \text{ at } 60^\circ\text{F}}{\rho_w \text{ at } 60^\circ\text{F}}$$

Where ρ_o at 60°F is the density of petroleum at 60°F

ρ_w is the density of distilled water at 60°F

It means that the specific gravity of petroleum is equal to the mass of a unit petroleum volume at 60°F to the mass of the same volume of water at 60°F.

The petroleum industry also uses another gravity term called API gravity degree which is defined as:

$$\text{Degree API} = \frac{141.4}{\text{sp. gr. @ } 60/60} - 131.5$$

Where: sp.gr. is the specific gravity at 60°/60°F.

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:

$$\text{Degree Baume} = \frac{140}{\text{sp. gr. @ } 60/60} - 130$$

The density of any liquid is a function of the temperature, there being expansion as the temperature rises therefore a reduction in the density. The variation of density is defined as:

$$\text{sp. gr. of oil at specific temp. } ^\circ\text{F} = \text{sp. gr. (60}^\circ\text{F/60}^\circ\text{F)} - \xi(t \text{ } ^\circ\text{F} - 60)$$

Where: SG at TF is the specific gravity at any temperature in °F.

ξ is the thermal expansion coefficient values of 0.000517- 0.000897.

5.2 Viscosity

Dynamic viscosity (μ) 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 in 1 sec (is the tangential force per unit area required to move one horizontal plane with respect to another plane) . In the cgs system, the unit of viscosity is the poise (gm/cm.s) or centipoise (0.01 P). Fluidity is simply the reciprocal of viscosity

Capillary Method

Many types of instruments have been proposed for the determination of dynamic viscosity. The simplest and most widely used are capillary types, and the viscosity is derived from the Hagen-Poiseuille equation:

$$\eta = \frac{\pi R^4 \Delta P t}{8 L V}$$

Where η is the absolute (dynamic) viscosity

ΔP is the pressure drop along the ends of capillary tube (gm/cm^2)

R radius of capillary tube (cm)

t the time of liquid flow through capillary tube (sec)

L the capillary tube length (cm)

V volume of flow liquid through capillary tube (ml)

Batch flow times are generally used; that is, the time required for a fixed amount of sample to flow from a reservoir through a capillary is the datum actually observed. Some of the principal capillary viscometers in use are those of Ubbelohde, Ostwald.

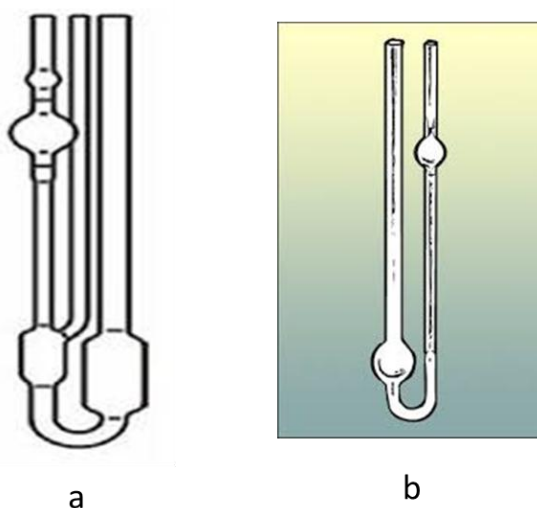


Figure 5 Glass capillary viscometers after a) Ubbelohde and b) Ostwald

Summary of Test Method ASTM D445

The time is measured for a fixed volume of the liquid to flow through the capillary viscometer under an accurately reproducible head and at a closely controlled temperature. The kinematic viscosity is then calculated from the measured flow time and the calibration constant of the viscometer.

Kinematic viscosity (ν): It is the dynamic viscosity in centipoises divided by the density at the same temperature:

$$\nu = \frac{\mu}{\rho}$$

Where ν is kinematic viscosity

μ is dynamic viscosity

ρ is the density

Kinematic viscosity has the unit of stoke (cm^2/sec), although centistokes (0.01 cSt) is in more common usage.

Saybolt Method

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

$$\nu = \frac{a \times \text{Saybolt } s + b}{\text{Saybolt } s}$$

Where a and b are constants.

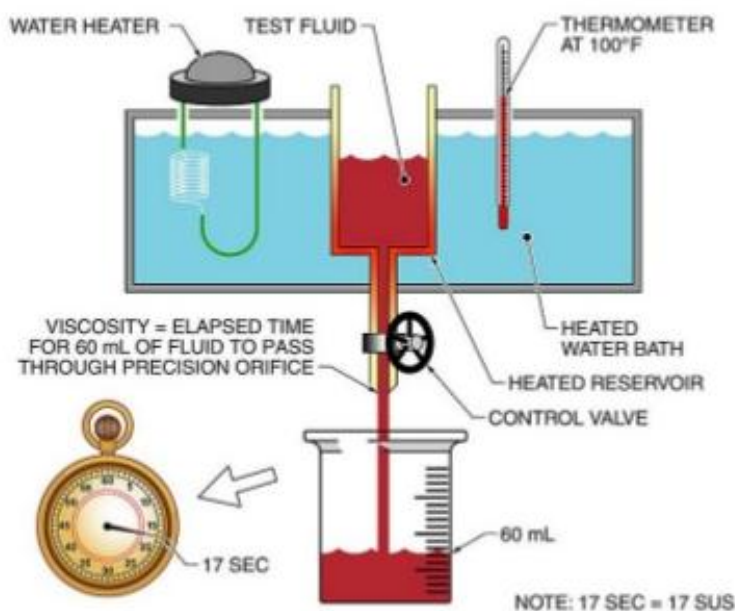


Figure 6 Saybolt viscometer



The relation of Petroleum Viscosity and Temperature

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:

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

Where v is kinematic viscosity in cSt, T is temperature in °K, 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 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.

Viscosity Index

The viscosity index (VI) is a parameter that indicates the rate of change of the oil viscosity due to a variation in temperature. This index is defined as the ratio of the difference of viscosity (U) of the lube oil to be used with respect to the viscosity (L) of petroleum (aromatic) oil having zero VI to the difference of viscosity (H) of high VI oil (paraffinic; 100 VI) to the viscosity (L) of zero VI oil for a temperature change from 38°C to 99°C. This can be written in the following way;

$$VI = 100 \frac{(L - U)}{(L - H)}$$

Where L , U , and H are the viscosities of the low VI reference oil ($VI = 0$), the sample oil, and the high VI reference oil ($VI = 100$), respectively, all at a temperature of 38°C. Note that the viscosity of the sample (U) and reference oils (L and H) must be so selected that they have the same viscosity at 99°C. This can be explained graphically as below:

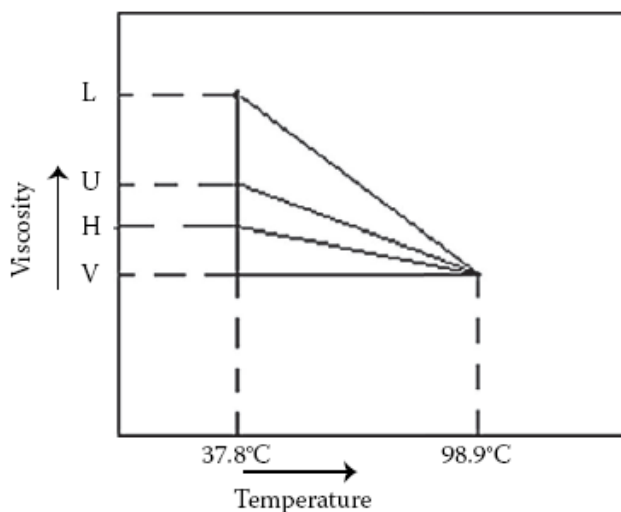


Figure 7 Graphical representation of the viscosity index.

The relation of Petroleum Viscosity and Pressure

The viscosity of petroleum fractions increases on the application of pressure, and this increase may be very large. The pressure coefficient of viscosity correlates with the temperature coefficient, even when oils 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 20,000 psi.

$$v_p = v_o c^p$$

Where v_p is the viscosity at pressure p
 v_o is viscosity at atmospheric pressure
 c is constant

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.

5.3 Melting Point and Freezing Point

In general melting point is the temperature at which material is converted from solid state to liquid state at 1 atm. while freezing point is the temperature at which material is converted from liquid state to solid state at 1 atm.

Melting point is a test that is widely used by wax suppliers and consumers. It is particularly applied to petroleum waxes that are rather highly paraffinic or crystalline in nature (ASTM D87); freezing point it is the temperature (TFZ) at which the crystals formed by cooling of petroleum and petroleum products.

There are some notes and factors that affecting these points:



1. The melting points of components of an oil increase with their molecular weight or number of C atoms as in Table-1.
2. The branched-chain hydrocarbons usually have melting points higher than their normal straight-chain compounds, whereas n-pentane melts at -130°C the 2,2-dimethylpropane thus melts at -20°C and whereas n-octane melts at -57°C 2,2,3,3-tetramethylbutane does so at 104°C . In contrast the phenomena are inverted for freezing point.

C atoms / molecule	Melting pint $^{\circ}\text{C}$	C atoms / molecule	Melting pint $^{\circ}\text{C}$
1	-182	20	36
5	-130	30	66
10	-30	40	82
15	10	50	92

Table 1 Melting Points of n-Paraffins

The cloud, pour, melting, and freezing points of petroleum and petroleum products are varied depending on the following:

1. These points will be raised as the molecular weight of petroleum increased.
2. These points will be raised as the coordination of hydrocarbon molecules increased.
3. These points will be raised as the hydrocarbon molecules are more saturated.

Hydrocarbon	No. of C atoms	Freezing point $^{\circ}\text{C}$
Butane	4	-138°C
Decane	10	-29.7°C
Tridecane	13	-6.2°C

Table 2 Freezing point of hydrocarbon

Notes

1. Pour point (T_p) and melting point (T_M) have limited uses in wax and paraffinic heavy oils to determine the degree of solidification.
2. For petroleum mixtures, there are ranges of melting and freezing points versus percent of the mixture melted or frozen. For a mixture, the initial melting point is close to the melting point of the lightest compound in the mixture, while the initial freezing point is close to the freezing point (or melting point) of the heaviest compound in the mixture.



5.4 Surface and Interfacial Tension

Surface tension is a measure of the attracting 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. Temperature and molecular weight have a significant effect on surface tension

The surface tension of petroleum and petroleum products has been studied for many years. The narrow range of value (approximately 24–38 dyn/cm) for such widely diverse materials.

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

Where σ in dyne/cm, K is the Watson characterization factor, sp.gr. is the specific gravity, and T is the temperature in K.

Petroleum Product	Surface Tension (dyne /cm)
Gasoline	26
Kerosene	30
Lube oil No. 10	32
Lube oil No. 50	34
Heavy Residue	37

Table 3 Surface tension of some petroleum products

From Table 3 it seems that value of surface tension increase with the increase of molecular weight of petroleum compounds.

The interfacial tension between oil and distilled water provides an indication of compounds in the oil that have an affinity for water. The measurement of interfacial tension has received special attention because of its possible use in predicting when oil (lube 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.

5.5 Molecular Weight

In principle, the relation between molecular weight of oil compounds and the average boiling point is well-known. The characterization of a crude oil or oil fraction requires determining a boiling range, which can be established by either (i) recording a distillation curve or, more simply, (ii) the temperatures at which 5%-95% of the total distillate have accumulated in a



receiver. Figure-8, illustrates the increase of boiling points with the increase of molecular weights among n-alkanes and condensed aromatics.

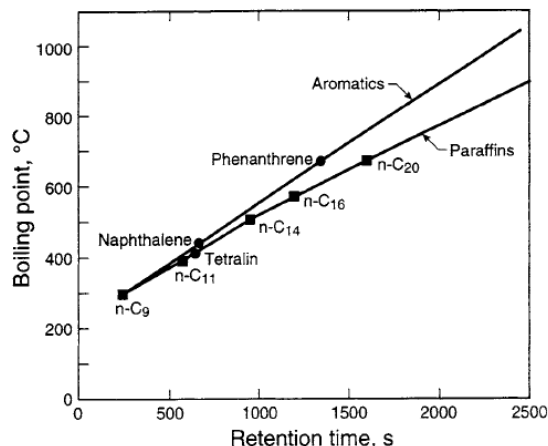


Figure 8 Hydrocarbon boiling points, determined from GC retention times.

5.6 Refractive Index

The refractive index is the ratio of light velocity in vacuum to light velocity in substance and expressed by:

$$n = \frac{C_o}{C_s}$$

Where C_o and C_s are the velocities of light in a vacuum and when passing through a substance and can be written as:

$$n = \frac{\sin i}{\sin r}$$

Where i is the angle of incidence and r the angle of refraction, both determined with incident light normal to the surface of the substance.

Refractive index normally used to estimate the density and the hydrocarbon composition for petroleum distillate by comparison with pure hydrocarbons.

°API	Density	n^a
6	1.029	1.566
22	0.918	1.509
44	0.802	1.448
58	0.742	1.417
72	0.691	1.390

Table 4 Relationships between API Density, and Refractive Index



The refractive index of oil is generally measured with a conventional (Abbe refract meter) and monochromatic Na-D light at 20°C (ASTM D-1218).

Under these conditions n ranges from 1.39 to 1.49, but depends on density or some covariant function. Among n -alkanes, n thus increases with the molecular weight (see Table 5); among oil fractions of similar average molecular weight, it increases sequentially from paraffinic to naphthenic and aromatic species; and among naphthenes and aromatics, it tends to be significantly higher for polycyclics than for the corresponding monocyclics.

C ₅ H ₁₂	1.3579	Eicosane	1.4425
C ₆ H ₁₄	1.3749	Cyclopentane	1.4064
C ₇ H ₁₆	1.3876	Cyclohexane	1.4266
C ₈ H ₁₈	1.3975	Cycloheptane	1.4449
C ₉ H ₂₀	1.4054	Benzene	1.5011
C ₁₀ H ₂₂	1.4119	Methylbenzene	1.4961
Nanodecane	1.4409	Ethylbenzene	1.4959
Propylbenzene	1.4920		

Table 5 Refractive Indices of Some Hydrocarbons Commonly Occurring in Crude Oils

3.6 Electrical Conductivity

The electrical conductivity of hydrocarbons is quite small. For example the normal hydrocarbons (hexane and up) have an electrical conductivity smaller than $10^{-16} \Omega^{-1}\text{cm}^{-1}$; benzene itself has an electrical conductivity of $4.4 \times 10^{-16} \Omega^{-1}\text{cm}^{-1}$ and cyclohexane has an electrical conductivity of $7 \times 10^{-16} \Omega^{-1}\text{cm}^{-1}$. It is generally recognized that hydrocarbons do not usually have an electrical conductivity larger than $10^{-18} \Omega^{-1}\text{cm}^{-1}$. Thus, the electrical conductivity of hydrocarbon oils is also small of the order of 10^{-19} to $10^{-12} \Omega^{-1}\text{cm}^{-1}$.

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 it is observed to increase exponentially with the latter. Most oils increase in conductivity with rising temperatures.