Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering Department

Properties of Petroleum & Natural Gas

Third Class

Lecture 17

By

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Physical and Chemical Properties of Crude Oil and Oil Products

Viscosity

The viscosity of oil is a measure of its resistance to internal flow and an indication of its oiliness in the lubrication of surfaces. There are two types of viscosity: dynamic and kinematics viscosity.

Kinematic viscosity (υ) = dynamic viscosity (μ) / density (ρ)

The unit of dynamic viscosity is poise (0.1 Pa·s). It is more commonly expressed, particularly in ASTM standards, as centipoises (cP). While the kinematics viscosity as centiStokes – cSt (10-6 $m^2 \cdot s^{-1}$). The following equations can be used to calculate the liquid viscosities of petroleum fractions at atmospheric pressure and at temperatures of 37.8 °C(100 °F) and 98.9 °C (210 °F)

$$\log \nu_{210} = -0.463634 - 0.166532(\mathrm{API}) + 5.13447 \times 10^{-4}(\mathrm{API})^2 - 8.48995 \times 10^{-3} K(\mathrm{API}) + \frac{8.0325 \times 10^{-2} K + 1.24899(\mathrm{API}) + 0.197680(\mathrm{API})^2}{\mathrm{API} + 26.786 - 2.6296K}$$

$$\log \nu_{100} = 4.39371 - 1.94733K + 0.127690K^2 + 3.2629 \times 10^{-4}(\mathrm{API})^2 - 1.18246 \times 10^{-2} K(\mathrm{API}) + \frac{0.17161K^2 + 10.9943(\mathrm{API}) + 9.50663 \times 10^{-2}(\mathrm{API})^2 - 0.860218K(\mathrm{API})}{\mathrm{API} + 50.3642 - 4.78231K}$$

where v_{100} and v_{210} are the kinematic viscosities at 100 and 210 °F, in centistokes. The viscosity can be measured by several instruments (U-tube Viscometer, Saybolt Universal Viscosity (SSU), thermo-viscosity, Red wood viscometer and Englar)

Thermo. = 15 + 148.5 kinematic Vis. = 46 SSU – 1183

The comparison of viscosity by different instruments is shown in Figure 1.

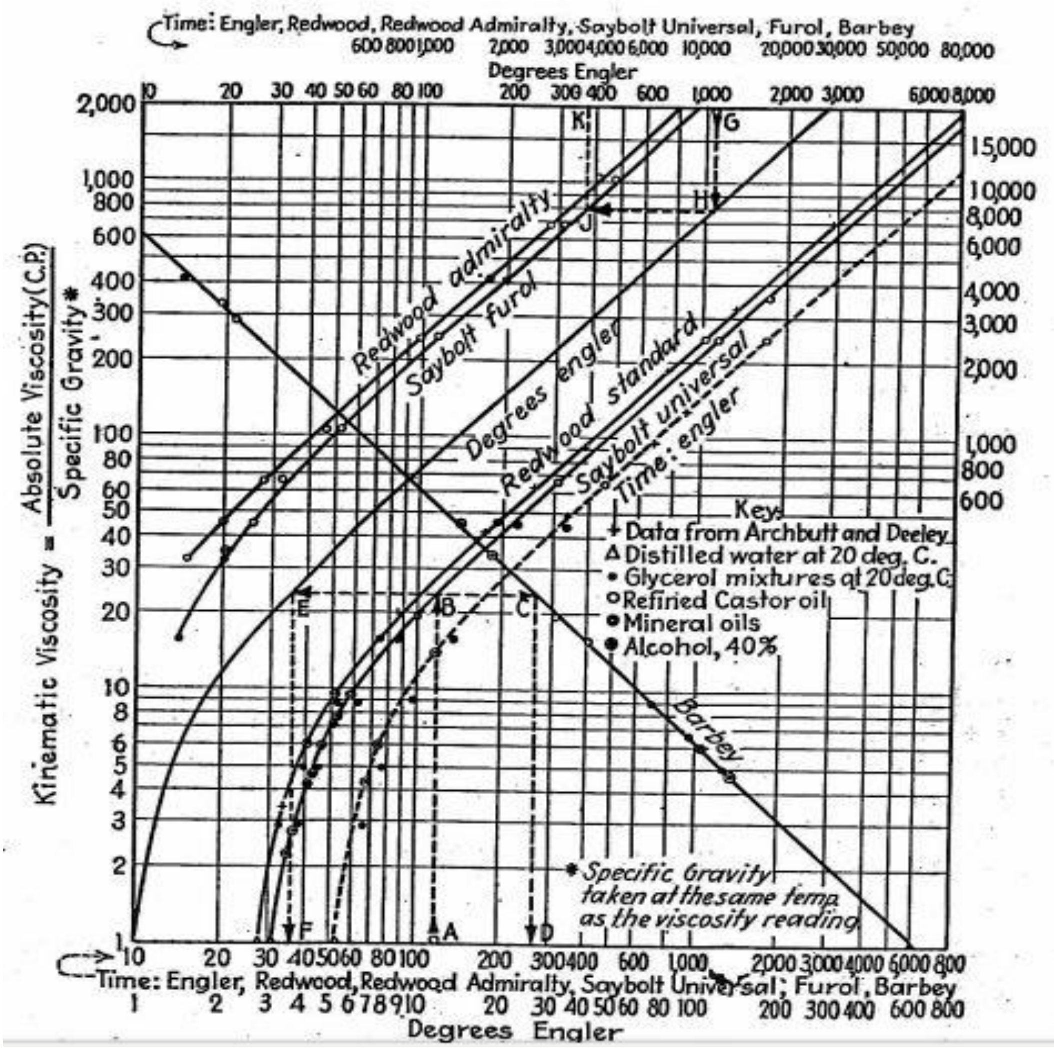


Figure1. Comparison of viscosity by different instruments (Viscosity must be at the same T).

Pour Point

The pour point is defined as the lowest temperature at which the sample will flow and is a rough indicator of the relative paraffinicity and aromaticity of the crude. A lower pour point means that the paraffin content is low and greater content of aromatics. To estimate the pour point of petroleum fractions from viscosity, molecular weight, and specific gravity, the following form is used for this purpose:

$$T_P = 130.47[SG^{2.970566}] \times [M^{(0.61235-0.47357SG)}] \times [\nu_{38(100)}^{(0.310331-0.32834SG)}]$$

Where Tp is the pour point (ASTM D 97) in kelvin, M is the molecular weight, and v_{38} (100) is the kinematic viscosity at 37.8°C (100F) in cSt. This equation was developed with data on pour points of more than 300 petroleum fractions with molecular weights ranging from 140 to 800 and API gravities from 13 to 50.

Carbon Residue, wt%

Carbon residue is determined by distillation to a coke residue in the absence of air. The carbon residue is roughly related to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the more valuable the crude. This is expressed in terms of the weight percent carbon residue by either the Ramsbottom (RCR) or Conradson (CCR).

Crude distilled (%) at 1100°F = 100 – 3*CCR

CCR is the Carbon residue for whole crude oil

Salt Content, lb/1000 bbl

If the salt content of the crude, when expressed as NaCl, is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing. If the salt is not removed, severe corrosion problems may be encountered. If residua are processed catalytically, desalting is desirable at even lower salt contents of he crude. Although it is not possible to have an accurate conversion unit between lb/1000 bbl and ppm by weight because of the different densities of crude oils, 1 lb/1000 bbl is approximately 3 ppm.

Sulfur Content, wt%

Sulfur content and API gravity are two properties which have had the greatest influence on the value of crude oil, although nitrogen and metals contents are increasing in importance. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5%. Crudes with greater than 0.5% sulfur generally require more extensive processing than those with lower sulfur content.

Flash point

Flash point TF, for a hydrocarbon or a fuel is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air with the presence of an external source, i.e., spark or flame. From this definition, it is clear that hydrocarbons with higher vapor pressures (lighter compounds) have lower flash points. Generally flash point increases with an increase in boiling point. Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile petroleum products (i.e., LPG, light naphtha, gasoline) in a high-temperature environment. The flash point can be estimated using the following equation:

$$T_F = 15.48 + 0.70704\, T_{10}$$

Where T10 is normal boiling point for petroleum fractions at 10 vol% distillation temperature. Both temperatures (T10 and flas point (TF) in Kelvin).

Notes:

- Flash point of petroleum fractions is the minimum temperature at which vapours arising from the oil will ignite, i.e. flash, when exposed to a flame under specified conditions.

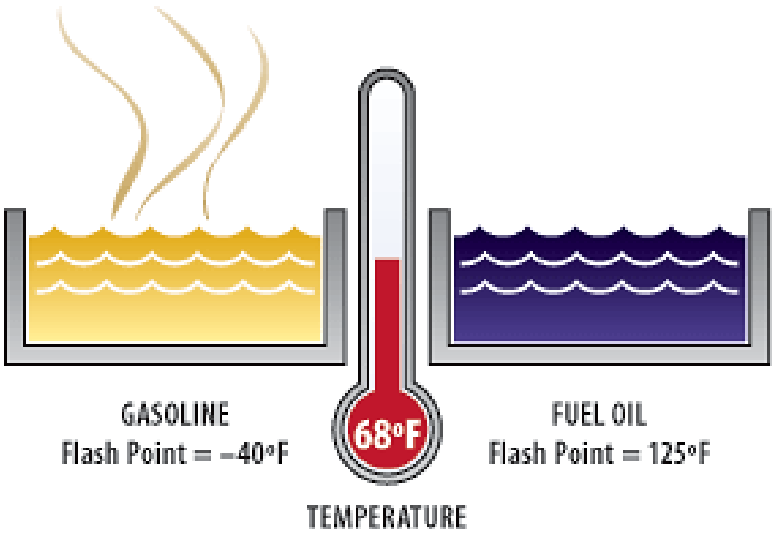
- The flash point indicates the maximum temperature that the fuel can be stored without serious fire hazard.

- Flash point is an important test for light petroleum fractions especially in high temperature environment and is directly related to the safe storage and handling of petroleum products.

- Flash point decreases with increasing volatility of fuel, i.e. the higher vapour pressure the lower is the flash point.

- Generally for crude oils with RVP greater than 0.2 bar the flash point is less than 20°C.

- High flash point means higher temperature is required for the fuel to flash. The fuel therefore does not ignite easily and is safe.



There are several methods of determining flash points of petroleum fractions.

• **The Closed Tag method (Abel) (ASTM D56)** is used for petroleum stocks with flash points below 80°C (175 °F).

• **The Pensky-Martens method (close cup) (ASTM D93)** is used for all petroleum products except waxes, solvents, and asphalts.

• **The Cleveland Open Cup method (ASTM D 92)** is used for petroleum fractions with flash points above 80°C (175°F) excluding fuel oil.

• This method usually gives flash points 3-6°C higher than the above two methods.

The main reason for the requirement of flash point test is to:

- Assess the fire hazards of a liquid hydrocarbon with regard to its flammability and then classify the liquid into a group.

- This classification is then used to warn of a risk and to enable the correct precautions to be taken when using, storing or transporting the liquid.

- The lower the flash point temperature, the greater the risk.

Fire Point

Fire point of petroleum fractions is the lowest temperature at which vapors arising from the oil will ignite, i.e. fire, when exposed to a spark or flame under specified conditions. Therefore, the fire point of a fuel indicates the maximum temperature that it must not reach it to prevent the combustion of the petroleum fractions.

Aniline Point

The lowest temperature at which an equal volume mixture of the petroleum oil and aniline are miscible is the aniline point. Since aniline is an aromatic compound, petroleum fractions with high aromatic content will be miscible in aniline at ambient conditions. Aniline point can be estimated using the following relation:

$$AP = -183.3 + 0.27(API)T_b^{1/3} + 0.317T_b$$

Where AP is in °C Tb is the mid boiling point in kelvin and API is API gravity.

Cetane number

The cetane number measures the ability for auto ignition and is essentially the opposite of the octane number. The cetane number is the percentage of pure cetane (n-hexadecane) in a blend of cetane and alpha methyl naphthalene which matches the ignition quality of a diesel fuel sample. This quality is specified for middle distillate fuels. Since determination of cetane number is difficult and costly, ASTM D976 (IP 218) proposed a method of calculation. Calculated number is called calculated cetane index (CCI) and can be determined from the following relation:

$$CCI = 454.74 - 1641.416SG + 774.74SG^2 - 0.554T_{50} + 97.083(\log_{10} T_{50})^2$$

WhereT50 is the ASTM D 86 temperature at 50% point in °C Another characteristic of diesel fuels is called diesel index (DI) defined as:

$$DI = \frac{(API)(1.8AP + 32)}{100}$$

Which is a function of API gravity and aniline point in °C.

Smoke Point

The smoke point is a test measures the burning qualities of kerosene and jet fuel. It is defined as the maximum height in mm, of a smokeless flame of fuel. The smoke point (SP) can be calculated using the following equation:

$$SP = -255.26 + 2.04AP - 240.8 \ln(SG) + 7727(SG/AP)$$

Where AP is the aniline point in °C and SG is the specific gravity at 15.5°C. Equation above estimates SP according to the IP test method. To estimate SP from the ASTM D1322 test method, 0.7 mm should be subtracted from the calculated IP smoke point.

Freezing Point

Petroleum fractions are mostly liquids at ambient conditions. However, heavy oils contain heavy compounds such as waxes or asphaltenes. These compounds tend to solidify at low temperatures, thus restricting flow. The freezing point is the temperature at which the hydrocarbon liquid solidifies at atmospheric pressure. It is one of the important property specifications for kerosene and jet fuels due to the very low temperatures encountered at high altitudes in jet planes.

Molecular Weight

Molecular weight (M) is perhaps the most important characterization parameter for petroleum fractions and many physical properties may be calculated from this parameter. M can be pridicted by using the following equation:

$$M = 42.965[\exp(2.097 \times 10^{-4} T_b - 7.78712 SG + 2.08476 \times 10^{-3} T_b SG)] T_b^{1.26007} SG^{4.98308}$$

This equation can be applied to hydrocarbons with molecular weight ranging from 70 to 700, which is nearly equivalent to boiling point range of 300-850 K (90-1050F) and the API gravity range of 14.4-93. For heavy petroleum fractions based on the molecular weight of heavy fractions in the range of 200-800:

$$M = 223.56 \left[\nu_{38(100)}^{(-1.2435+1.1228SG)} \, \nu_{99(210)}^{(3.4758-3.038SG)} \right] SG^{-0.6665}$$

The three input parameters are kinematic viscosities (in cSt) at 38 and 98.9°C (100 and 210F shown by $v_{38}(100)$ and $v_{99}(210)$, respectively, and the specific gravity (SG) at 15.5°.