Module 1: History of Fuels

Lecture 5: Fundamental definitions, properties and various measurements

Keywords: Properties, vaporization, octane number, cetane number, calorific value

1.3 Fundamental definitions, properties and various measurements

1.3.2 Definitions and properties of liquid and gaseous fuels

The composition of petroleum varies with the location, age and also individual well. The high proportion of carbon and hydrogen indicate that hydrocarbons are the major constituents of petroleum. The principal types of hydrocarbon present in crude oil are normal, branched or cyclic saturated hydrocarbons, aromatic hydrocarbons or compounds with molecular structure associating both these basic types.

The properties of crude petroleum and its fractions can be determined by various ways.

Crude oils are roughly classified into different bases according to the nature of principal type of hydrocarbons present in it. The bases are paraffin base, naphthene based, mixed base or intermediate base and aromatic base. Paraffin based crude oils composed of mainly paraffins. Mixed base or intermediate base crudes are lower in n-paraffins and higher in naphthenes compared to that of the paraffin base oils. Naphthene base crudes are characterized by a high percentage of naphthenes and almost no presence of any wax. Aromatic base crudes contain a relatively high percentage of the lower aromatic hydrocarbons. This classification is arbitrary, but long use of this concept makes this classification valuable to the technical persons.

^{0}API or API gravity is an empirical correlation which is actually a representation of specific gravity of petroleum crude or cuts (fractions). It is defined by American Petroleum Institute (API), as,

$$API\ gravity = \frac{141.5}{sp.gr.\left(\frac{15.5^o}{15.5^oC}\right)} - 131.5$$

API gravity is used in petroleum chemistry instead of specific gravity. This is because; the petroleum cuts are having specific gravities which are very near to each other. But use of API gravity makes the difference of gravity wider between the two consecutive cuts, as specific gravity is in the denominator in the expression of API gravity.

Vaporisation characteristics of petroleum cuts are obtained by distilling a definite volume of the fraction in a specified apparatus. As petroleum cuts are the mixture of different hydrocarbons, they do not have a definite boiling point, but have a boiling range. Initial boiling point (IBP) of a petroleum cut is the temperature when first drop of distillate comes out of the condenser of the distillation apparatus. Final boiling point (FBP) is the maximum temperature recorded at the end of the distillation. Distillation cannot be carried on beyond 350^0C temperature at atmospheric pressure, because at this temperature, cracking of the hydrocarbons starts. Boiling range of a petroleum cut is important in evaluating it.

Viscosity index is a property of petroleum fractions, which is defined as the rate of change of viscosity with temperature. This is indicated by a number in an arbitrary scale ranging from 0 to 100, higher the number more is the viscosity index. A viscosity index of 100 means, oil which ideally does not become thin at elevated temperatures or become viscous at lower temperature. Mainly paraffinic base lubricating oils exhibit a viscosity index near 100.

Flash point and fire point are the two important properties of petroleum fractions. Flash point is defined as the minimum temperature at which the fuel upon heating evolves vapour which after mixing with the air give a sudden flash when a source of fire is brought in contact with it. Fire point is the minimum temperature at which the fuel vapour in admixture with air will produce a continuous fire when a fire source is brought in contact with the vapour. So, the fire point is more than the flash point for a particular petroleum fraction. Hence, flash point is more important than fire point in view of any fire hazard.

During the transportation of heavy oil fractions in pipelines, there is a possibility of freezing the oil within the pipe when it is transported at cold climate. Here **pour point and cloud point** are the two properties of these oils which play important role. Pour point is the maximum temperature, at which oil ceases to flow when it is cooled at specified condition. Pour point is reported by adding 2.8^0C or 5^0F to this temperature, which is a caution to technical people. Cloud point is the temperature at which oil becomes cloudy, when it is cooled at a specified condition.

Burning quality of kerosene can be determined by its illuminating capacity and it is expressed by two properties, smoke point and char value. Smoke point is defined as the maximum flame height in millimeters when kerosene burns in a standard apparatus without producing any smoke or shoot. Char value is the amount of char produced in milligrams on the wick of a standard apparatus per kilogram of kerosene burned.

Carbon residue is the important characteristic of the oils which are used in engines, burners and furnaces. The carbonaceous residue obtained after heating the oil at a specified rate due to cracking and decomposition is called carbon residue. Two different types, Conradson and Ramsbottom carbon residue were determined, depending on the methods followed.

Octane number determines the quality of gasoline or petrol. When gasoline is burned in a spark ignition engine (petrol engine), it produces power. A good quality gasoline burns smoothly without making any noise in the engine. Whereas, burning of a bad quality gasoline is not smooth and produces a sudden high pressure by burning all fuel at a time, which forms pressure wave or detonation or knock to the engine. The octane number of a gasoline is a measure of knocking tendency. Octane number is determined by comparing the performance of a model fuel and the gasoline under test in a standard engine in laboratory. The model fuel is prepared by mixing iso-octane (2,2,4 trimethyl pentane) whose octane number is assumed to be 100 and n-heptane, whose octane number is assumed to be zero. So, octane number of a gasoline sample is defined as the percent by volume of iso-octane in a model fuel (mixture of iso-octane and n-heptane) whose knocking performance matches with the test gasoline. Hence, a gasoline with octane number 90 means, its knocking tendency matches with a model fuel having 90 vol% iso-octane. The descending order of octane number of the hydrocarbons is: aromatics> iso-paraffins> naphthene> olefins> n-paraffins. There are many octane number improver. Tetraethyl lead (TEL) is the most common improver. Now-a-days, octane number is improved by adding alkylates to gasoline.

Ignition quality of diesel is expressed by **cetane number**. Diesel is injected in the hot compressed air in the cylinder of a diesel engine, which then burns to produce power. If there is a large time gap between the injection and ignition, there is an unwanted accumulation of fuel in the cylinder, which suddenly burns at a time with a pressure wave, producing diesel knock. Like octane number, here also a model fuel is prepared by mixing n-hexadecane or cetane (whose cetane number is assigned to 100) and ∞-methyl naphthalene (whose cetane number is assumed to be zero), at different volume proportions. The performance of the diesel under test is compared with the model fuel. The percent by volume of n-hexadecane in a model fuel is the cetane number of the test diesel whose diesel knocking performance matches with the model fuel when tested in a specified engine. Hence, if the performance of test diesel matches with the performance of the model fuel having 45/55 blend of cetane and ∞-methyl naphthalene, then the diesel is assigned to cetane number of 45. The descending order of cetane number of hydrocarbons is just reverse to that of octane number.

Aniline point is also a property mainly of diesel. This is defined as the temperature at which the oil under test is completely miscible with equal volume of aniline, when tested in a standard apparatus. Aromatics dissolve aromatics easily. Hence, if the oil contains more aromatics, its aniline point will be low. But if the oil contains more paraffin, its aniline point will be more.

Diesel index is an empirical index which is defined as

$$Diesel\ index = \frac{Aniline\ point, ^{o}F \times Degree\ API}{100}$$

Usually, it is observed that diesel index is three units higher than the cetane number, although it is not exactly the same for all the cases.

Petroleum cuts contain ash but to a very negligible amount. Moisture content is also very less which can be determined by standard test. Sulfur in petroleum oils remain in the form of sulfides, disulfides, marcaptans, thiophenes and higher thiophenes. Heavier the cut more is the sulfur content.

Calorific value of both petroleum oil and gaseous fuel are determined by bomb calorimeter and Junker's calorimeter. The gross calorific value of petroleum cuts vary from 10000 to11500 kcal/kg, the lower boiling cut, such as gasoline shows higher value and heavier oils show lower value. Among gaseous fuels, natural gas and LPG has highest calorific value, which is in the range of 43000 to 46000 kJ/m^3. Other gaseous fuels are of moderate or low calorific value, such as the calorific value of producer gas, carbureted water gas and coal gas are 5000, 19000 and 20,000 kJ/m^3 respectively.

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