Lecture 16: Properties and Testing of Petroleum Products

Hello, and welcome to the lecture number 16 of Petroleum Technology. In this lecture, we will talk about the properties and testing of petroleum products. We know that petroleum crude can give us a variety of petroleum products that are boiling in different boiling ranges and their compositions are different because their hydrocarbon contents are different. So, their properties also go on getting differ from one another. So, not a single set of test procedures is suitable to evaluate all of them. Everyone has their own properties; hence, the test procedures may differ from one another.

Indian standard specifications for various petroleum products determine the marketable petroleum grades. In the end, we have to market the petroleum fractions and make them suitable as market products by setting standard specifications as per each country's requirements. Our country also has Indian standard specifications, known as IS specifications. Each of the petroleum products has its particular IS specification based on its properties.

First, let's talk about the property-specific gravity. Specific gravity represents the weight by volume, and due to the similarity in the inherent chemical composition of different petroleum products, it is challenging to correlate their specific gravity with other parameters. For example, one petroleum grade may have a specific gravity that is almost similar to the next grade. So, two consecutive grades may have similar specific gravity, and relying solely on specific gravity makes it difficult to distinguish between them. This is because one petroleum grade's hydrocarbon range at the higher boiling point is almost similar to the hydrocarbon range just below it, whose initial hydrocarbons are similar to their higher hydrocarbons. Therefore, specific gravity alone is not an ideal measure for distinguishing between petroleum fractions. That's why API gravity is introduced, which is represented in degrees API, calculated using the formula: API gravity = 141.5 / (specific gravity at 60°F/60°F) - 131.5. This formula is used to represent the gravity of any petroleum grade. As you can see, specific gravity is in the denominator, which magnifies small differences between specific gravities. Thus, API gravity is used to distinguish between adjacent fractions based on their gravity. Now, let's discuss viscosity. Viscosity is an important property of all liquid grades, measuring their resistance to flow. Typically, viscosity is measured in centistokes, which is the kinematic viscosity, and it is determined in the laboratory for various petroleum grades. Viscosity varies from one grade to another, and different standard viscometers are used to measure viscosity. These viscometers follow specific standard procedures. Generally, viscosity is determined by measuring the time it takes for a specific petroleum liquid to flow through a standard orifice at a defined temperature. The time, measured in seconds, represents the viscosity.

Engler, Redwood Number 1, Redwood Number 2, Seybold Universal, and Seybold Furor are all standard viscometers used for determining the viscosity of petroleum liquids. Engler is an apparatus where the same volume of oil and water is taken, and their flow times are measured. The unit used for Engler is the degree Engler, which represents the ratio of the time elapsed by the oil and water. This time is then converted to centistokes using a specific formula. Similarly, Redwood Number 1, Redwood Number 2, Seybold Universal, and Seybold Furor also represent viscosity values in centistokes. Viscosity is a crucial property for transportation fuels such as gasoline and diesel, as well as for fuel oil used in burners and lubricating oils, among other applications.

Gasoline and diesel, which are used as transportation fuels, are injected into the automobile engine in a piston-cylinder arrangement. If the viscosity of these fuels is too high, making the liquid thicker, it becomes difficult to inject the oil into the automobile engine's cylinder. Conversely, if the viscosity is too low, there is a problem with the oil dripping down from the cylinder. Therefore, it is crucial to maintain the right viscosity for these oils.

For fuel oil used in burners, atomization is required for fuel efficiency. If the viscosity of the fuel oil is very high, it becomes difficult to atomize the oil in the burners, leading to reduced burner efficiency. Lubricating oil should also have a specific viscosity. It is essential that lubricating oil maintains its viscosity because it is used for lubrication purposes. The viscosity index is an important property for lubricating oil. The effectiveness of lubricating oil in a particular system depends on its viscosity, and the relationship between viscosity and temperature is denoted by the viscosity index. The viscosity index is defined as the rate of change of viscosity with temperature.

Lubricating oil is used in machine parts that are in motion, and moving machine parts are always subject to friction. To prevent friction and dissipate heat at these moving parts, lubricating oil is applied. If, at a certain temperature, the lubricating oil loses thickness or viscosity is reduced, the oil may drip from the moving parts, defeating the purpose of lubrication. Therefore, it is crucial that lubricating oil maintains its viscosity even as the temperature rises. This property is expressed in terms of the viscosity index, which measures the rate of change of viscosity with temperature. A low rate of change of viscosity with temperature ensures that the lubricating oil can effectively serve its lubrication purpose.

The viscosity index is expressed on a scale of 0 to 100, where a higher viscosity index indicates better quality lubricating oil. In other words, if the viscosity index approaches 100, the lubricating oil is of higher quality. The property known as viscosity gravity constant is used for crude oil and is represented by the formula: $10G - 1.0752 * \log(V - 38) / 10 - \log(V - 38)$, where G is the specific gravity at 60 degrees Fahrenheit, and V is the viscosity at 100 degrees Fahrenheit. This property is determined for crude oil.

Now, let's discuss the distillation range. The distillation range is considered the identity of a petroleum product because each petroleum product has a characteristic boiling range. The boiling range of gasoline differs from that of diesel, and likewise, the boiling range of lubricating oil differs from that of kerosene. The distillation range of a petroleum distillate product serves as its distinguishing characteristic. By determining the boiling range of an unknown oil, you can assess whether the oil has been adulterated or not.

The distillation range specification is essential for distillate products like gasoline, kerosene, and various other products. It helps in identifying and characterizing these products. In distillation tests for petroleum products, a measured volume of oil is distilled in a batch mode at a specified rate. In laboratory tests for measuring the distillation range of petroleum cuts, the standard ASTM distillation method D 86 is used.

The standard method for determining the distillation range of any petroleum cut involves using a batch distillation apparatus to construct a distillation curve that relates the percentage distilled to temperature. Different points on the curve are recorded as characteristic values of the distillate cut. The initial boiling point and final boiling point are among these characteristics.

The initial boiling point is the temperature at which the first condensed drop emerges from the tip of the condenser, and this temperature is measured. The final boiling point is the highest temperature reached during the distillation process. Additionally, the mid-boiling cut or mid-boiling temperature is another characteristic where the temperature at which 50 percent of the distillate has been collected is measured.

The figure shows the distillation apparatus following the ASTM standard ASTM D 86. In this setup, a round-bottom flask is placed inside a chamber with a burner to heat the distillation flask. A specific quantity of oil, such as 100 ml, is taken for the distillation, whether it is gasoline or kerosene. A thermometer is inserted through a cork from the top, and another side limb extends into a condenser bath. This condenser bath has a tube through which vapors pass, condense, and form drops that exit from the tip of the condenser. The temperature at which the first drop emerges from the condenser tip is recorded as the initial boiling point. It's important to note that the thermometer bulb should be positioned at the junction of the limb and the neck of the round-bottom flask.

In this process, a liquid petroleum product is heated, causing it to boil. The vapor rises from the liquid's surface, comes into contact with the thermometer bulb, and then flows through the limb to the condenser. The thermometer bulb measures the temperature of the vapor, and some of the vapor may condense on the thermometer bulb before falling back into the liquid. This process can be considered a form of reflux distillation. The remaining vapor passes through the condenser tube and is collected as distillate. The distillate is collected by volume, and the volume is measured at intervals of, for example, every 5 or 10 degrees Celsius as the temperature increases. This measurement provides data on the volume of distillate collected at various temperatures, resulting in a distillation curve, often referred to as an ASTM distillation curve.

The provided picture shows the actual apparatus, with the distillation flask in the foreground and the condenser behind it. The tip of the condenser leads to the collector, where the liquid distillate is gathered. The knob visible in the image is used to control the heater temperature. Now, moving on to another property determination: Reed vapor pressure. This property is primarily measured for gasoline distillates. Gasoline is the lightest boiling liquid in the petroleum cut series and may contain lower boiling hydrocarbons. These lower boiling hydrocarbons, when dissolved in the gasoline distillate, can potentially lead to vapor locking issues in transportation lines or within the piston-cylinder arrangement of automobile engines. Therefore, gasoline distillates must have a defined vapor pressure. If the vapor pressure exceeds a certain limit, stripping may be necessary to remove the lighter boiling components.

To measure the vapor pressure that gasoline can exert, this experiment is conducted. It serves as a measure of the volatility of gasoline distillate. The quantity of gaseous hydrocarbons or low-boiling components dissolved in gasoline depends on the degree of weathering of the oil or the pressure at which it is collected. This test allows for the measurement of any lighter boiling materials present in the gasoline. It's important to note that the true vapor pressure is typically higher than the Reed vapor pressure by 5 to 9 percent. The provided image illustrates the equipment used for measuring Reed vapor pressure according to ASTM standards.

This is the standard equipment: a water bath with water inside, equipped with a temperature controller and indicator. The water is heated to around 37.8 degrees Celsius or 100 degrees Fahrenheit. The Reed vapor pressure apparatus consists of a thick steel bomb into which a specific quantity of gasoline is placed. A steel tube with a pressure gauge is attached to this assembly. The entire assembly is filled with gasoline and then immersed in the heated water bath for a period of time, allowing the gasoline inside the bomb to reach the water temperature. Once the gasoline inside the bulb reaches 37.8 degrees Celsius, it is removed from the water bath and shaken upside down several times to ensure any lighter vapor enters the vapor space. This vapor space is monitored by the pressure gauge, which provides the reading of the Reed vapor pressure (RVP) for the sample. The RVP of a mixture is experimentally determined according to a procedure standardized by the American Society for Testing and Materials (ASTM) at 100 degrees Fahrenheit (37.8 degrees Celsius). This method is used to measure the RVP of gasoline.

Now, let's discuss other important properties: flash point and fire point. The flash point is defined as the minimum temperature at which a given oil releases just enough vapor to create an inflammable mixture with air, indicated by a momentary flash when an external source of fire is introduced to the vapor. In an apparatus (as shown), a specified quantity of oil is heated according to standard procedures, and a sample flame is introduced into the vapor space by opening a shutter on the apparatus's lid. If the flash point is reached, this sample flame will produce a momentary flash.

You understand that the flash point is an indication of the fire risk of the oil. The momentary flash indicates that up to this temperature or below, the oil can be heated without igniting. On the other hand, the fire point is the minimum temperature at which oil vapor will continue to burn instead of just flashing, signifying a more significant fire hazard. For the same product, the fire point is naturally higher than the flash point. Thus, the flash point is more crucial than the fire point because it provides an early warning of potential fire risks.

Both the flash point and fire point should be measured and reported for any type of oil. They offer valuable information for the storage and transportation of fuels. For instance, gasoline, which contains many lighter boiling materials, has a very low flash point, typically around 23 degrees Celsius or even less. This is why gasoline is considered a highly dangerous and flammable fuel. In contrast, kerosene may have a flash point ranging from 23 to 66 degrees Celsius, depending on its composition. Heavier fuels like diesel or fuel oil have flash points greater than 66 degrees Celsius.

Hence, these oils are considered safe due to their higher flash points. Depending on the type of liquid product and its flash point, storage and transportation designs should be tailored accordingly. Various apparatus are used to determine the flash point and fire point, including the Penske-Martin apparatus, Abel apparatus, and Cleveland open cup apparatus.

The Penske-Martin apparatus is suitable for oils with flash points above 50 degrees Celsius, such as fuel oil or lubricating oil. The Abel apparatus is used for oils with flash points below 50 degrees Celsius, such as kerosene. Both of these are closed-cup apparatuses, meaning they have a sealed cup for testing.

The Cleveland open-cup apparatus is employed when dealing with very high-boiling or heavy oils, such as crude oil or certain residues. However, flash points obtained from open cup apparatus may be less accurate than those obtained from closed cup apparatus, as there is potential for vapor escape in open cup testing.

Now, moving on to the pour point and cloud point. These properties are particularly important for fuel oil, lubricating oil, diesel oil, and similar products that are transported or stored in cold environments. The pour point is defined as the temperature, typically 5 degrees Fahrenheit or 2.8 degrees Celsius, higher than the temperature at which the oil stops flowing when cooled under specific conditions.

During the transportation of heavy oils like lubricating oil, fuel oil, or diesel oil across different regions or countries, temperature changes can cause issues. In colder climates, the oil may become so cold that it solidifies and stops flowing within the transportation pipelines or storage tanks. In such cases, heating methods must be employed to maintain the oil's fluidity and ensure it continues to flow. This is where understanding the pour point becomes crucial.

The pour point is determined in a laboratory using a standard apparatus. This apparatus involves lowering the temperature of a sample of oil and observing at which temperature the oil completely freezes, making it impossible to pour. The pour point is determined by adding a cautionary value of 2.8 degrees Celsius or 5 degrees Fahrenheit to the freezing temperature. For example, if the freezing point of an oil is 2 degrees Celsius, the pour point would be 4.8 degrees Celsius (2 degrees Celsius + 2.8 degrees Celsius).

The addition of 2.8 degrees Celsius or 5 degrees Fahrenheit serves as a cautionary measure. When the pour point approaches, typically around 5 degrees Celsius (in the example given), it signals that heating appliances may be needed to maintain oil flow through pipelines. In general, a lower pour point is desirable for any oil because it indicates that the oil can flow more easily without the need for external heating. The cessation of flow at low temperatures occurs due to two main reasons: an increase in viscosity and the formation of wax crystals inside the oil. These wax crystals originate from the straight-chain paraffinic compounds present in heavy oils. At lower temperatures, these wax crystals begin to form, leading to an increase in the oil's viscosity, which can cause it to become sluggish or seize up within transportation lines.

Next, we have the cloud point, which is defined as the temperature at which an oil becomes cloudy when cooled in a specified manner. The cloud point is higher than the pour point. When an oil is cooled, a point is reached where haziness or cloudiness appears on the oil's surface. This cloudiness may be caused by factors such as moisture or the formation of small wax crystals. The cloud point marks the beginning of the cessation of flow or the oil's tendency to become less fluid as it gets colder.

So, cloud point is more important than pour point. Asphaltic substances act as pour point depressants by inhibiting the wax crystal growth. There are several types of pour point depressants; one example is asphaltic substances.

Next, coming to the freezing point can be defined in two ways. One definition is that the freezing point is the temperature at which crystals of hydrocarbons formed during cooling disappear. That is, by heating, whenever oil is totally frozen, that means it is solidified. If you heat the oil and measure the temperature at which the crystals of hydrocarbon just disappear, that is the freezing point temperature. In another way, we can represent the freezing point as the temperature in degrees Celsius at which the oil just loses its ability to flow because of continuous cooling down. This occurs through cooling.

Another property to consider is the congealing point, which is determined only for petroleum wax. This is the temperature at which the molten wax becomes solidified. How is it done? It is done by applying a drop of molten wax to a thermometer bulb and noting the temperature at which it congeals or solidifies when the thermometer is rotated under standardized cooling conditions. This method is suitable for all types of waxes.

So, this is a property of waxes. Now, coming to smoke point and char value. Smoke point and char value are two properties that apply only to kerosene, and they represent the burning quality of kerosene as an illuminant or as a fuel. The smoking tendency of kerosene is determined by the smoke point test, and the deposit-forming tendency is determined by the char value test. What is the smoke point?

Imagine a lantern where a flame is created using a wick, and there is kerosene in a container at the bottom. The length of the wick can be regulated by a device. As the wick length increases, the flame length will also increase. Eventually, you will notice a sooty tail forming at the end of the flame. If you reduce the flame length, the soot formation will decrease, resulting in a smooth, rounded flame.

The smoke point is defined as the maximum flame height in millimeters to which kerosene can burn without producing smoke in a standard apparatus. The standard apparatus consists of a stand with a kerosene holder, where kerosene is placed. On top of the holder, there is a wick, and at the back of this apparatus, there is a mirror scale. This mirror scale has graduations, and in front of it, there is a lead glass panel that is closed during the experiment. There is a device to adjust the flame height in such a way that it produces the longest flame without any soot or black smoke formation. The height of the flame is then measured using the mirror scale from behind.

So, this is how the smoke point experiment is conducted. A good-quality kerosene shows a smoke point of 20 to 25 millimeters, and there are specifications for the smoke point in the Indian standard specification for kerosene.

Now, let's discuss the char value. The char value also represents the burning quality of kerosene. The char value is the amount of char in milligrams for every kilogram of kerosene burnt, which is formed on the wick of a standard lamp burning under prescribed conditions.

In this ASTM standard burning lamp, a specific quantity of kerosene is taken within the container, typically around 1 kilogram or another specified amount. There is a standard wick and a standard glass chimney. The wick is burned, and the lamp is positioned so that the flame is at its optimum condition, with maximum height and no soot formation. The lamp is kept in this state for 24 hours, and after that time, the amount of kerosene consumed is weighed.

The difference in weight will indicate the amount of kerosene consumed, and it will be observed that the length of the flame has been reduced, with char forming on the tip of the wick. This char is removed by scraping it into a watch glass and weighed. This measurement gives the char value, represented in terms of milligrams of char per kilogram of kerosene burnt. The char value of high-grade kerosene should not exceed 20 milligrams per kilogram.

To clarify, a good kerosene should have a high smoke point and a low char value. In addition to char formation after 24 hours, there will also be a whitish or grayish bloom formation inside the glass chimney. This bloom formation is a representation of the burning quality of kerosene and occurs due to the presence of disulfides in the kerosene. The reduction in flame height is also measured using a graduated scale inside the standard glass chimney. All of these factors, when considered together, provide an assessment of the burning quality of kerosene.

These are the references. Thank you for your attention.