Lecture 19: Properties and Testing of Petroleum Products (Contd.)

Hello, and welcome to lecture number 19 of Petroleum Technology. In this lecture, we will learn about the properties and testing of petroleum products. At the beginning, let us discuss the ash content of petroleum products. Usually, the petroleum product does not produce any ash. Even if it produces ash that is very low, such as residual fuel oils, it shows a maximum of 0.1 percent ash.

The distillate should ideally have zero ash content, but certain additives in gasoline and diesel fuels can lead to the formation of ash. Typically, distillate products do not contain any measurable ash content. However, some distillates are upgraded by adding various additives, which can result in the formation of a small amount of ash after the fuel is burned. To determine the ash content, a known sample is ignited, and the carbonaceous residue left behind is heated to 800 degrees Celsius in a muffle furnace. After cooling, the residue is weighed to determine the ash content, following a similar procedure as used for coal to determine its ash content.

The same procedure is followed for liquid fuels, but the ash recovered is usually very low and may not be detectable at all.

The refractive index is another important property of liquid fuel. This test method covers the measurement of the refractive index of transparent and lightly colored hydrocarbons. Petroleum products must be transparent and lightly colored for their refractive index to be determined accurately. The measurement is typically done within the range of 1.33 to 1.5 at temperatures between 20 degrees and 30 degrees Celsius, using either manual or automatic procedures. The test method may not be applicable to liquids that are strongly colored because in very dark-colored liquid products, light cannot easily pass through them, and their refractive index value becomes difficult to measure. Now, let's discuss the moisture content of petroleum products.

While the solubility of water in oil is quite low, ranging from 0.005 to 0.5 percent, some petroleum products may still contain moisture, often in the form of an emulsion. In certain petroleum oils, moisture can be present in concentrations of up to 1 percent. The presence of water in oil is undesirable because it reduces the calorific value of the fuel, deteriorates its burning quality, and can lead to an uneven and inefficient combustion process.

The Din and Stark method is employed for determining the moisture content in oil. This method is based on ASTM standards and provides an accurate measurement of low water content, typically ranging from 50 to 1000 ppm in oils. It utilizes an electrometric titration method with specific standards.

Let me describe the Din and Stark method: This method determines moisture content by distillation using an immiscible solvent such as xylene or toluene. The apparatus consists of a glass round-bottom flask and a condenser.

The condenser is a special type with an extension at the bottom known as a trap, which is a graduated tube. When the oil in the flask is heated, vapors rise and enter the condenser. In the condenser, these vapors are condensed, and any water present in the oil is collected in the trap. The remaining vapor flows down through the condenser line and refluxs back into the flask. There are water inlet and outlet connections on the condenser for cooling purposes. The apparatus consists of a glass flask that is heated using suitable means, typically a mantle heater, and it is equipped with a reflux condenser that discharges into a trap, which is then connected to the flask. The trap serves to collect and measure the condensed water and return the solvent to the flask.

To calibrate the equipment, the efficiency of the apparatus is measured initially. Calibration is performed by taking 50 milliliters of toluene in the round-bottom flask and intentionally adding a measured amount of water, for example, 5 ml of water, to the 50 ml of toluene. The toluene-water mixture is then distilled and heated for a specific time period, such as 30 minutes, which is assumed to be sufficient to collect all the evaporated water in the trap. In the trap, both water and toluene are collected, but there is a phase separation between the two, with water at the bottom and toluene at the top. The volume of water accumulated in the graduated trap is measured. It is important to note that not all of the water added to the toluene will make its way into the trap; some may be lost in the process.

After the specified time, let's assume it's 30 minutes or 45 minutes; the amount of water collected in the trap is measured, say it's 4.9 ml. To represent the efficiency of the apparatus or calibration, you can calculate it as follows: (4.9 / 5) * 100, which may result in an efficiency of around 97 percent or 98 percent for the entire apparatus.

Now, the toluene and water system are discarded. In a new system, which is dried and prepared, take the same 50 milliliters of toluene and 50 milliliters of your sample, which could be kerosene or diesel. Once again, intentionally add 5 ml of water to this system. We assume that this kerosene contains a small amount of inherent water, and we don't know its exact quantity. The entire liquid system is then distilled, just as in the previous experiment, for the same duration, such as 30 minutes or 45 minutes. Observe how much water accumulates in the trap; let's say it's 5.1 ml.

So, you added 5 ml of water at the beginning of the experiment, and you collected 5.1 ml in the trap. The difference, 5.1 ml - 5 ml, is 0.1 ml of water that must have come from the kerosene. However, it's important to consider that the efficiency of the system is not 100 percent. To determine the actual amount of water present in the 50 ml of kerosene, you multiply the observed 0.1 ml by the efficiency, which is 98 percent. This will give you the accurate amount of water present in the kerosene. So, we need to express this in terms of the percentage of water present in kerosene. This is the process for determining the water content in kerosene using the Dean and Stark method.

Now, let's discuss the cetane number, which is important for diesel fuel. Diesel fuel is primarily used in compression ignition engines, also known as CI engines. In a CI engine, the fuel vapor is injected into a piston-cylinder arrangement within the cylinder. The hot air inside the cylinder is compressed, and at a specific compression ratio, the entire mixture of fuel vapor and hot air ignites. However, there is a time lag or delay period between the injection of diesel fuel into the hot, compressed air and its ignition. This delay is quite natural because when fuel vapor is injected into the hot, compressed air within the cylinder, the piston is compressing the mixture, and ignition occurs only at a certain compression ratio. So, there is a time gap between the start of injection and the start of ignition of the diesel fuel. If this delay period is excessively long, there will be an accumulation of too much fuel in the cylinder, leading to an overly rapid combustion process.

In certain abnormal situations, there can be instances where, despite piston compression, the fuel doesn't ignite immediately. In such cases, the next phase of fuel injection occurs into the same fuel vapor and air mixture, and compression continues. This leads to a significant accumulation of fuel in the cylinder, which subsequently burns very rapidly all at once. This rapid combustion generates a shockwave or thrust within the diesel engine, resulting in a phenomenon known as "diesel knock." The rapid increase in cylinder pressure is what causes the diesel knock, and it can be detrimental to the diesel engine. The cetane number serves as a measure of the propensity for diesel knock, and it is an important factor for diesel engine performance. The delay period during which ignition occurs is inherently linked to the type of hydrocarbon used and is also influenced by the composition of the diesel fuel. A higher cetane number indicates a shorter delay period and better ignition quality, while a lower cetane number suggests a longer delay period and a higher likelihood of diesel knock.

The preferred order of decreasing ignition quality for diesel fuels is as follows: normal paraffins > olefins > naphthenes > isoparaffins > aromatics. This order is the reverse of the order used for measuring gasoline anti-knock quality. In this ranking, normal paraffins have the highest ignition quality or the highest resistance to knocking, while aromatics have the lowest ignition quality or the highest tendency to knock. To measure the ignition quality of diesel fuel and determine its cetane number, a scale is used. Normal hexadecane, also known as cetane (C16H34), is assigned a cetane number of 100, representing the highest ignition quality. On the other hand, an aromatic compound like alpha-methyl naphthalene is assigned a cetane number of 0, representing the lowest ignition quality. This scale ranges from 100 to 0, similar to the octane number scale used for gasoline. The cetane number of a diesel fuel sample is determined by comparing its ignition quality to blends of two reference fuels (cetane and alpha-methyl naphthalene) in a standard engine. The percentage by volume of cetane in the reference fuel that matches the ignition quality of the sample diesel is considered the cetane number of the diesel fuel. For example, if the ignition quality of the diesel matches that of a 46% blend of cetane and alpha-methyl naphthalene, the cetane number assigned to the diesel fuel is 40.

The cetane number of a diesel fuel is a critical factor for its performance in diesel engines. The ideal cetane number for a diesel engine depends on the type of engine and its operating conditions. For low-speed diesel engines, typically found in applications like heavy-duty trucks, a cetane number in the range of 25 to 30 is sufficient for good performance. However, high-speed diesel engines, which operate at higher engine speeds (e.g., 1500 rpm or more), require diesel fuel with a higher cetane number, typically in the range of 45 to 55, to ensure optimal performance. The cetane number is inversely related to the ignition delay period. In other words, fuels with higher cetane numbers have shorter ignition delay periods. This property is desirable because it leads to more uniform and controlled fuel ignition inside the engine cylinder, resulting in better engine performance.

High cetane number fuels are particularly beneficial in cold weather conditions. They make it easier to start compression ignition engines in cold climates and facilitate faster engine warm-up. Cold weather can make it challenging to vaporize and ignite diesel fuel, but fuels with high cetane numbers help overcome these challenges. To improve the cetane number of diesel fuels that contain high levels of aromatics and isoparaffins (which tend to lower ignition quality), cetane number improvers or enhancers can be added. These additives include alkyl nitrates, carbamates, peroxides, and other compounds that enhance the ignition properties of the fuel. In summary, the cetane number is a key indicator of diesel fuel quality and ignition performance in compression ignition engines. Higher cetane numbers are generally preferred for better engine performance, especially in high-speed diesel engines and cold weather conditions.

The aniline point is a measure of the miscibility of a liquid, such as diesel fuel, with an equal volume of aniline, which is an aromatic compound. In the context of diesel fuel, a higher aniline point temperature indicates better suitability and quality of the diesel fuel for ignition in compression ignition engines (diesel engines). This is because high-quality diesel fuel typically contains a higher proportion of isoparaffins and normal paraffin and a lower proportion of aromatics.

Here's how the aniline point test works and why a higher aniline point is desirable for diesel fuel quality: Components of Diesel Fuel: Diesel fuel is a complex mixture of hydrocarbons. It can contain various components, including paraffin, isoparaffins, naphthenes, and aromatics. Aromatics vs. Normal Paraffin: Aromatics are a class of hydrocarbons characterized by the presence of one or more aromatic rings (e.g., benzene rings). Normal paraffins are straight-chain hydrocarbons with no aromatic rings. Isoparaffins are branched-chain hydrocarbons. Miscibility with Aniline: In the aniline point test, a sample of diesel fuel is mixed with an equal volume of aniline. Aromatic compounds tend to dissolve more readily in aniline, while normal paraffins require higher temperatures to become soluble in aniline. Higher Aniline Point: If the diesel fuel has a higher aniline point temperature, it suggests that it contains a greater proportion of normal paraffins and fewer aromatics. This is desirable because high-quality diesel fuel typically has a higher content of normal paraffins, which are good for ignition quality, and a lower content of aromatics. Better Ignition Quality: Diesel fuels with more normal paraffins tend to have better ignition quality and are preferred for use in compression ignition engines. They ignite more easily and smoothly, contributing to better engine performance and reduced emissions. In summary, a higher aniline point temperature in diesel fuel indicates a better quality fuel with a higher proportion of normal paraffin and a lower proportion of aromatics. This composition is desirable for good ignition quality in diesel engines, leading to improved engine performance and reduced environmental impact.

The diesel index is an empirical index calculated from the aniline point temperature of diesel fuel. It is expressed as the aniline point in degrees Fahrenheit multiplied by the degree API (American Petroleum Institute gravity) divided by 100. Numerically, the diesel index is typically around 3 units higher than the cetane number. This index provides an approximation of the cetane number of the diesel fuel.

To determine the aniline point of diesel fuel, an ASTM standard method is used. Here's how the aniline point is measured: Sample Preparation: A specific volume of aniline (usually 10 milliliters) and an equal volume of the diesel fuel sample are taken in a glass test tube. It's essential to ensure that the thermometer bulb does not touch the walls of the test tube. Stirring: A stirrer is inserted into the test tube to ensure uniform mixing of the aniline and diesel throughout the test. Heating Bath: The test tube containing the aniline and diesel mixture is placed in a larger glass container, often a beaker, filled with glycerin. The glycerin serves as a heating bath. The purpose of the glycerin bath is to provide gentle and controlled heating to the mixture. Heating: The glycerin bath is slowly heated, and the heat is transferred to the aniline-diesel mixture. Continuous stirring ensures that the two components mix thoroughly. Monitoring Temperature: Throughout the heating process, the temperature of the mixture is monitored using a thermometer inserted into the test tube. Aniline Point Determination: The aniline point is reached when the mixture of aniline and diesel just becomes completely miscible (fully dissolved). This is the temperature at which the aniline point is measured. The resulting temperature, measured in degrees Fahrenheit, is the aniline point of the diesel fuel. This value is then used to calculate the diesel index, which provides an empirical indication of the cetane number and ignition quality of the diesel fuel. A higher diesel index suggests better ignition quality, making the fuel more suitable for use in compression ignition engines (diesel engines).

One time will come when one temperature will come and continuously, the temperature should be recorded in the thermometer. One temperature will come when it will be seen that the aniline and diesel are both completely miscible to each other, making a single phase. Previously, aniline, which is a dark red-colored liquid, forms a separate phase with diesel. After heating up to a certain degree of temperature and under stirring, both the liquid phases get miscible to each other, forming one liquid phase. At this condition, the heating source is removed and the whole system is put under cooling and cooling is done at a rate of 1 to 3 degrees centigrade per minute.

While cooling under stirring at a temperature, it will be observed turbidity starts to produce within the liquid mixture in the test tube and that temperature is noted. Whenever the whole liquid becomes turbid, that temperature is called the aniline point and that is the temperature when again the phase separation will start. So, the mixture after cooling the temperature at which two phases separate is recorded as the aniline point and in fact, two phases start to separate when turbidity starts to produce. The foaming tendency of oil is another unwanted situation when the oil lubricants produce foam after it is applied to an application point. High surface tension co-foaming in lubricating oil can be a significant issue as it negatively impacts the performance of the lubricant. When air is introduced into the lubricating oil, it can form a foam layer on metal surfaces. This foam layer prevents the formation of a complete lubricating oil film on the surface, which, in turn, reduces the lubricating oil's effectiveness. Additionally, the intrusion of air can lead to oxidation of the lubricating oil, further degrading its performance.

There are several factors that can contribute to foam formation in lubricating oil, including high surface tension contaminants. Contaminants can also contribute to entraining air and forming bubbles in the lubricating oil. The consequences of foam formation include incomplete oil films, low oil pressures, and accelerated oil degradation, including the depletion of additives. Therefore, it's crucial to assess the foaming tendency of lubricants before their application to ensure optimal performance in various systems.

The foam test is used to measure the foaming tendency of a lubricant. This test helps determine whether a lubricating oil has a tendency to foam, which can be problematic in systems such as high-speed gearing, high-volume pumping, and splash lubrication, where maintaining a good oil film on surfaces is essential for effective lubrication. The foam test method is standardized by organizations like ASTM to ensure consistent and reliable evaluation of lubricant foaming characteristics. Contaminants in lubricants, as well as air entrained in use oils, create bubbles and foam.

The foam test is conducted by taking two different portions of the oil sample and placing them in two separate glass containers. In each container, a diffuser is inserted to facilitate the introduction of air into the oil. These two containers are maintained at two distinct temperatures: one at 24 ± 0.5 degrees Celsius and the other at 93.5 ± 0.5 degrees Celsius. A constant rate of airflow is maintained through the oil using the diffuser, with a rate of 94 ± 5 milliliters per minute for a duration of 5 minutes. After this 5-minute period of air bubbling, the supply of air is stopped or closed. Subsequently, the foam produced on the surface of the oil is measured.

Before measuring the foam height and volume, the container is allowed to sit undisturbed for an additional 10 minutes. During this period, the behavior of the foam is observed. If the oil has a tendency to produce foam, the foam generated during the air-sparging process will persist on the surface of the oil. On the other hand, if the foaming tendency of the oil is low, the foam will gradually diminish over the 10-minute period. By measuring the foam height and volume at the end of both the initial 5-minute period of air sparging and the subsequent 10-minute resting period, the foaming characteristics of the oil can be assessed and evaluated. This test helps determine the oil's ability to resist or control foam formation, which is important in applications where foam can negatively affect lubrication and performance.

These are the references. Thank you for your attention.