

Lecture 17: Properties and Testing of Petroleum Products (Contd.)

Hello, and welcome to the lecture number 17 of petroleum technology. In this lecture, we will again talk about the properties and testing of petroleum products. Now, let us come to the carbon residue. All petroleum products contain hydrocarbons and as we go on to the higher boiling range hydrocarbons or higher boiling range petroleum products, they produce after burning the carbonaceous material. So, this property carbon residue property is important for oils used in gas production, in diesel engines, in burners and for lubricating oils used in motors. These are this carbon residue is important for those oils that are heavy and at the same time they are used at higher temperature applications.

So, at higher temperatures, there is a tendency for oils to burn and form a carbonaceous precipitate or carbonaceous residue. When an oil is heated, it undergoes evaporation and cracking sets in; this is the decomposition process. Heavier, more complex compounds can form carbonaceous deposits known as carbon residue. Naturally, these residues have a very high percentage of carbon and very little hydrogen. There are two methods for determining this residue: the Conradson and Ramsbottom methods.

Usually, the Conradson test is performed for fuel oils, while the Ramsbottom test is used for lubricating oil. Here is the apparatus for the Conradson carbon residue test: an iron crucible is used, into which a measured quantity of heavy oil is placed and weighed. The crucible is then placed in a stand, and a burner is set beneath it to provide heat. Sometimes, at higher temperatures, the oil inside the iron crucible may catch fire. After all the fuel oils in the crucible have been exhausted, a carbon residue deposit can be observed at the bottom of the crucible. The crucible is then weighed again, and this measurement provides the carbon residue formation of that oil. Carbon residue is typically represented as milligrams of carbon residue per milliliter of oil. Similarly, for the Ramsbottom carbon residue test, a furnace is used, and these are ASTM standard furnaces. The Ramsbottom furnace has small grooves at the top, where glass capsules are perfectly fitted inside.

In these glass capsules, there is a capillary through which heavy oil, such as lubricating oil, is injected and then weighed to measure the amount of oil taken. The furnace is maintained at 550 degrees Celsius, and several of these glass capsules are placed inside the grooves. These samples are quickly heated to the point where all the volatile matter evaporates out of the bulb through the capillary.

After a certain amount of time, when all the bulbs are free of any liquid oil and only carbon residues are left, they are taken out using tongs, cooled, and each one is weighed. The average of the carbon residue formed is then represented as the carbon residue of that oil. The remaining residue is calculated as a percentage of the original sample,

representing the carbon residue. This is how the carbon residue test is conducted in the Ramsbottom furnace.

Now, let's discuss the gum content of gasoline. Gasoline is often stored in refineries in storage tanks known as floating head storage tanks. In these tanks, gasoline can come into direct contact with the air because the lead is floating on the top of the gasoline surface. There is a slight difference in the rim diameter between the storage tank and the lead, creating a thin space. This space allows any volatile vapors to escape, reducing the risk of accidents. Gasoline can thus come into direct contact with atmospheric air, which can lead to the formation of gum.

During storage, certain classes of hydrocarbons, mostly olefins and diolefins (which are double-bonded hydrocarbons), are highly susceptible to reacting with the oxygen in the air, even at ambient temperatures. This reaction leads to the formation of sticky, resinous, polymeric gum. These polymeric compounds are commonly referred to as deposits or gums. They accumulate within the storage container, on the surface of the container's metal body, and may even float in the gasoline. These gums can pose various difficulties in automobile engines. They can clog the piston-cylinder system, lead to engine wear, and have adverse effects on engine efficiency, performance, emissions, and durability. Simultaneously, when gum forms in gasoline, the fuel loses important components, namely olefins and diolefins, which serve as octane enhancers.

In this manner, when gum forms, the gasoline's density increases, the boiling range expands, aromaticity rises, and simultaneously, olefinicity decreases. All of these factors reduce the quality of gasoline. Therefore, gum formation has a negative impact on gasoline properties.

The following table provides some terms and definitions related to gum formation:

Existent Gum: This refers to the gum that remains in the container after the fuel has evaporated in a specified furnace, without any further treatment. **Insoluble Gum:** Insoluble gum is the portion of existent gum that, when washed with a specific solvent, remains as gum that is not soluble in that solvent. **Soluble Gum:** Soluble gum is the part of the gum that is soluble in the chosen solvent after washing.

The potential gum is the sum of soluble and insoluble gum. Existent gum represents the gum that has already formed during the storage of a specific volume of gasoline, while potential gum represents the gum potential of a given gasoline to form additional gum. This chart provides a simplified description of gasoline, which contains components such as paraffins, naphthenes, aromatics, olefins, and very trace amounts of heteroatoms such as sulfur, nitrogen, oxygen, etc. When oxygen reacts with these components, hydroperoxide radicals are formed, which serve as precursors to oxidation. This oxidation process generates both soluble and insoluble oxidized products, both of which are

considered gums. These gums act as nucleating agents, leading to the formation of larger, sticky materials. Over time, these gums can settle and form sediment in storage tanks. When gasoline is used under various thermal conditions, such as in automobiles, these gums can adhere to surfaces and create deposits. This summarizes the overall fuel stability process.

Hence, gum is a highly undesirable component of gasoline. This image shows the ASTM standard gum content test apparatus. The bent nozzles are air nozzles through which hot air is passed into a glass container that holds a measured quantity of gasoline. To obtain an average result, several groups of containers are placed inside a heater, which operates at around 45 to 50 degrees Celsius. Within these groups, standard beakers containing measured quantities of gasoline are inserted. The bent nozzles are attached to the mouth of the beaker and supply air from an air compressor. When the air is allowed to pass and the heating continues for a certain duration, such as 20 minutes or half an hour, all the gasoline will evaporate, and any gum present in the gasoline will be deposited at the bottom of the container. These containers are then removed using tongs, allowed to cool, and weighed again.

This process provides the gum content of that particular gasoline, and the gum content is typically represented in terms of milligrams of gum per 100 milliliters of gasoline. The gum content of all six beakers is averaged to represent the gum content of the gasoline. Now, let's turn to one of the most crucial properties that we need to determine, which is the sulfur content of any petroleum product. Crude oil contains sulfur, and as crude oil is distilled, the lighter boiling fractions contain fewer sulfur compounds or low-boiling sulfur compounds compared to the higher boiling fractions. Consequently, sulfur exists in various forms of compounds in both crude oil and its distillate cuts.

These compounds include disulfides, sulphides, mercaptans, thiophenes, and their higher molecular weight derivatives. As crude oil is distilled, the lighter cuts contain lighter hydro-sulfur compounds, while heavier sulfur compounds are found in cuts with higher boiling points. High-boiling cuts contain larger, higher molecular weight sulfur compounds. Upon combustion of the fuel, these sulfur compounds form objectionable sulfur oxide gases that pollute the environment. It's important to note that sulfur dioxide, which is produced by burning fuel, contributes to environmental pollution.

Hence, sulfur content should be reduced in any oil used for combustion purposes. Laboratory determination of sulfur content in a fuel is best done using the bomb method. This method allows for the measurement of the sulfur present in liquid fuel. The determination of sulfur content in petroleum oil by the bomb method is used for petroleum products that are not highly volatile and contain at least 0.1 percent sulfur. In this method, a sample is oxidized through combustion in a bomb containing pressurized oxygen. In the next slide, you can see the bomb itself, which is a thick steel body. It has a

lead with two openings for inserting electrodes and a pinch cock for introducing oxygen into the bomb. There is also a crucible holder made of platinum. A platinum wire runs between the two openings, and a cotton thread extends from the wire down to the liquid fuel, ensuring the entire thread is moist with the liquid oil. When an electric current is passed through the electrodes, it ignites the cotton thread, which then ignites the liquid fuel. Inside the bomb, a small amount of water, typically around 10 to 15 ml, is present. After burning, the petroleum oil releases sulfur dioxide gas, which is absorbed into the water. After the entire assembly cools down, the bomb is removed, and the process is completed in a calorimeter.

The bomb is taken out of the calorimeter, cooled, and opened. Oxygen should be removed by pinching the cock. Then, the water inside the bomb is collected in a beaker, and the bomb is washed several times with distilled water. All the washings are collected in a beaker and treated with a standard barium chloride solution. Barium chloride reacts with sulfurous acid to form barium sulfate. This barium sulfate is then gravimetrically filtered and weighed, and by back-calculation, the amount of total sulfur present in the liquid fuel can be determined. This is how we determine the total sulfur content in petroleum oil using the bomb method. Another method for determining sulfur content is the lamp method or wick bolt method. In this method, volatile petroleum products, mainly LPG, are used to determine their sulfur content. LPG is burned in an atmosphere consisting of 70 percent carbon dioxide and 30 percent oxygen. After burning, the SO_2 produced reacts with H_2O_2 to form sulfuric acid. This sulfuric acid is then titrated against NaOH to determine the amount of sulfuric acid formed, and from there, the amount of sulfur present in LPG is determined.

This method can be applied to products with sulfur content ranging from 1 to 10,000 milligrams per kilogram, making it suitable for substances with high sulfur content. It is particularly useful for distillates with a total sulfur content of fewer than 300 milligrams per kilogram. The method can also be used to determine the volatile sulfur in substances supplied to the burner in the gaseous state after vaporization from the liquid phase, as is the case with LPG, where the volatile sulfur content is determined using the lamp method.

The lamp method is not suitable for determining the sulfur content in heavy-duty engine oils. In other words, it cannot be used to determine the sulfur content in heavy oils. Now, let's discuss the Doctor's test. The Doctor's test helps determine how sour petroleum oil is. Sour petroleum oil contains mercaptans and dissolved hydrogen sulfide. By definition, a stock is considered sweet if it passes the Doctor's test. This test is used to determine whether petroleum oil contains mercaptans and dissolved hydrogen sulfide.

In this process, mercaptans, hydrogen sulfides, and elemental sulfur are converted into oil-soluble sulfur compounds. However, it doesn't significantly remove sulfur from the

oil. In fact, mercaptans and hydrogen sulfide are responsible for the foul smell of petroleum oil. This process transforms the foul smell of the oil into a sweet smell, which is why it's referred to as a sweetening process. It's important to note that this process doesn't remove sulfur from the oil; it is not a desulfurization process.

The oil sample is shaken with an equal volume of sodium plumbite solution and a small amount of sulfur. When an oil cut contains mercaptans, the mercaptans will initially react with sodium plumbite to form oil-soluble lead mercaptides. These mercaptides, upon further reaction with elemental sulfur, form sweet-smelling, oil-soluble disulfides and result in a black precipitate of lead sulfide. Let's look at the equations:

$\text{RSH (Mercaptan)} + \text{Sodium Plumbite Solution} \rightarrow \text{Lead Mercaptide}$

$\text{Lead Mercaptide} + \text{NaOH} \rightarrow \text{Disulfide} + \text{Lead Sulfide Precipitate}$

If the test does not produce even a dark discoloration at the interface, the sample is considered sweet. In other words, if there is no dark discoloration at the interface between the oil and the sodium plumbite solution, it means that the oil does not contain mercaptans or hydrogen sulfide.

The processes that convert foul-smelling stocks into sweet-smelling or odorless petroleum products are known as sweetening processes. The Doctor's test is a test used to determine the presence of mercaptans and hydrogen sulfide in the oil, but the overall process that transforms foul-smelling compounds into sweet-smelling ones is referred to as a sweetening process.

These are the references. Thank you for your attention.