Lecture 18: Properties and Testing of Petroleum Products (Contd.)

Hello, and welcome to the lecture number 18 of Petroleum Technology. In this lecture, we will learn about the properties and testing of petroleum products. Here, at the beginning, we will talk about the octane number or octane rating of gasoline. Gasoline is used in an internal combustion engine, which is a spark ignition engine with reciprocating pistons. Here, the fuel is injected into the cylinder and in admixture with air, it gets burnt by a spark generated from a spark plug. So, here is what happens: the chemical energy of the fuel is converted into mechanical energy by burning the fuel and we get the shaft work.

The maximum power is derived from gasoline when it burns silently and relatively slowly in an automobile engine. To achieve this, a smooth and controlled combustion process is essential. When fuel vapor is injected into the engine cylinder and mixed with air, it forms a combustible mixture. Ignition of this mixture occurs when it reaches its flammability limit in the presence of a spark plug. This controlled ignition process results in a smooth and efficient release of power.

However, under certain engine conditions, combustion may start smoothly but then transition into a situation where the unburned fuel mixture ignites rapidly all at once. This phenomenon is known as detonation. In detonation, the entire unburned fuel mixture ignites spontaneously in a continuous and uncontrolled manner. This sudden and localized burning generates a high-pressure wave in the engine cylinder, leading to knocking or pinging noises. Knocking in a gasoline engine is undesirable and can result in a loss of power, engine damage, and reduced engine lifespan. To prevent knocking, gasoline needs to have a specific resistance to this phenomenon. Gasoline formulations are carefully designed to resist knocking and ensure a smooth and efficient combustion process. The antiknock quality or resistance of a fuel is measured in a standard engine and expressed as its octane number.

The antiknock quality of a fuel is determined by comparing its performance to that of two standard reference fuels in a standardized engine test. This test helps assess the fuel's ability to resist knocking and ensures that it meets the required octane rating standards, which are critical for the efficient operation of internal combustion engines.

The octane number of gasoline is determined by comparing its knocking tendency with that of synthetic mixtures containing iso-octane (2, 2, 4-trimethyl pentane) and normal heptane at different volume ratios. The goal is to find a synthetic mixture that matches the antiknock quality of the sample gasoline.

Here's how the process works:

Synthetic Mixtures: Synthetic mixtures are prepared using iso-octane and normal heptane at various volume ratios. These synthetic mixtures serve as reference standards with known octane ratings. Testing: The sample gasoline is tested in a standard engine to measure its knocking tendency. The knocking tendency is determined by observing the engine's behavior and the occurrence of knocking or pinging noises during combustion. Comparison: The knocking tendency of the sample gasoline is compared to the knocking tendencies of the synthetic mixtures. If the knocking tendency of the sample gasoline matches that of a specific synthetic mixture, then the octane number of that synthetic mixture is considered equivalent to the octane number of the sample gasoline. Octane Rating: The octane number of the sample gasoline is expressed as a percentage by volume of iso-octane in the synthetic mixture that provided the matching knocking tendency. For example, if the sample gasoline's knocking tendency matches that of a synthetic mixture containing 90% iso-octane and 10% normal heptane, then the octane number of the sample gasoline is 90.

The octane number is expressed on a scale from 0 to 100, where 0 represents normal heptane (poor antiknock quality), and 100 represents iso-octane (excellent antiknock quality). Aromatics have the best antiknock quality among hydrocarbons, while isoparaffins, naphthenes, and normal paraffins follow in descending order in terms of antiknock quality.

You've correctly pointed out that aromatics have a higher carbon-to-hydrogen (C/H) ratio compared to isoparaffins, and this difference in chemical structure plays a significant role in the antiknock quality of gasoline. Aromatics are hydrocarbons with closed unsaturated ring structures (e.g., benzene rings), which means they have fewer hydrogen atoms per carbon atom than iso-paraffins. The higher C/H ratio in aromatics leads to carbon deposits or "carbon fouling" during combustion, which can be detrimental to engine performance and emissions. While iso paraffin is selected as the reference standard for an octane rating of 100 on the scale, aromatics do indeed contribute to the overall antiknock quality of gasoline. Gasoline formulations aim for a balance between various hydrocarbon components to achieve the desired octane rating and engine performance. Higher concentrations of isoparaffins and other high-octane components are often used to improve antiknock quality while minimizing the negative effects associated with aromatics. In summary, the choice of iso paraffin as the reference standard for the octane rating scale is primarily based on their antiknock performance and stability in combustion, especially when compared to aromatics, which can lead to carbon deposits in the engine. However, it's important to maintain a balanced composition of hydrocarbons in gasoline to achieve the desired antiknock quality while meeting other performance and emission standards.

You've provided an accurate explanation of how certain additives, such as tetraethyl lead, can increase the octane number of gasoline and reduce engine knocking. Tetraethyl lead, for example, functions as an anti-knock agent by forming radicals that react with the fuel and oxygen, effectively delaying the combustion process. This delay in combustion prevents premature ignition, reducing the likelihood of knocking.

The relationship between octane number and the activation energy of the fuel is essential to understand why higher octane fuels require more energy to ignite. An increase in the octane number indicates a fuel's improved resistance to knocking or autoignition. In practical terms, this means that higher-octane fuels can withstand higher levels of compression in an engine before spontaneously igniting. As a result, more energy, in the form of heat or pressure, is needed to reach the ignition point and initiate combustion. This property is crucial for engines with higher compression ratios, such as those found in high-performance or turbocharged engines, as they require fuels with higher octane ratings to prevent knocking and achieve optimal performance. Lower-octane fuels are more likely to experience premature ignition, leading to knocking and potential engine damage. Therefore, the choice of gasoline with an appropriate octane rating is essential to match the engine's design and optimize performance while preventing knocking and other undesirable combustion effects. Additionally, the use of additives like tetraethyl lead or other modern alternatives can further enhance the anti-knock properties of gasoline.

A prolonged occurrence of engine knocking can cause serious damage to the engine's inner parts. Here, if you see this picture, it is a smooth burning whenever it is smooth and uniform burning in the piston cylinder. This is the piston and this is inside the cylinder. This is the spark plug and whenever the spark plug generates a spark, the whole of the fuel is burned in a uniform way, but whenever this knocking occurs, we will find the local burning of the fuel and local pressure rises very high and high heat transfer occurs. So, it generates high temperatures as well. This high pressure and high temperature in the engine gives a thrust to the engine, which is knocking.

The most common type of octane rating worldwide is the research octane number. Research octane number is the octane number which is measured at normal conditions, not severe conditions and at a low-speed engine. Research octane number is determined by running the fuel through a specific test engine with a variable compression ratio under controlled conditions and comparing these results with those for mixtures of isooctane and normal heptane. This is the usual measurement of octane number in a standard engine, as usually is done by comparing the knocking tendency with a mixture of isooctane and normal heptane. Another type of octane rating is called motor octane number MON or aviation lean octane rating.

Here, the motor octane number is a better measure of how the fuel behaves when under load. The motor octane number is measured in the same standard engine as we do for the research octane number but with a preheated fuel mixture, variable ignition timing, and higher engine speed. That means it stresses the knocking resistance of the fuel more.

Under this condition, the motor octane number is measured, and depending on the composition of the fuel, the motor octane number of modern gasoline is about 8 to 10 points lower than the research octane number. This is because the motor octane number is obtained under conditions that are more severe than the conditions for the research octane number.

It is possible for a fuel to have a research octane number greater than 100 because isooctane is not the most knock-resistant substance available. I have already mentioned that isooctane is taken as a standard with a 100 octane number, but there are several compounds that may have better performance than isooctane. Some aromatics also fall into this category, but there are several other compounds as well. So, whenever it is observed that some other compounds or fuels can perform better than isooctane, their performance is denoted by another name called octane performance or performance number. Thus, for substances with higher shock resistance, the octane performance is an extrapolation of the octane performance chart, and some sources mention the adoption of a performance number. It is observed that usually, the performance number is assigned to some fuels such as racing fuel, ethanol, or aviation fuel, as well as LPG, etc.

These substances have much higher or better performance than isooctane. The performance number is used to estimate the knocking characteristics of aviation gasoline with an octane number higher than 100. So, aviation fuel or aviation gasoline is actually considered a fuel with an octane number greater than 100. The standard reference fuels for knock ratings above 100 octane number are isooctane and its blend with tetraethyl lead. It's important to note that only isooctane is not used to measure the performance number or octane performance of fuels with an octane number higher than 100.

Instead, a blend of isooctane and tetraethyl lead is used to increase the octane number or the anti-knock ability of the fuel to more than 100. The performance number scale is based on engine power output. The following chart provides the octane ratings for some substances: Normal heptane: 0 octane number. Normal octane (in the same homologous series but at a higher molecular weight): octane number minus 10. Normal hexane (higher molecular weight in the homologous series): octane number 25. Normal pentane (a lower molecular weight hydrocarbon than normal heptane): octane number 62. Cyclohexane (a closed-ring saturated naphthene compound): octane number much higher, 97. I hope these corrections help clarify your text. If you have any further questions or need additional assistance, please feel free to ask.

Isooctane, as it is known, has an octane number of 100. Benzene, being an aromatic compound, boasts an octane number of more than 100, specifically 101. Methane, a very small molecule, and ethane both exhibit much higher octane ratings than isooctane. Toluene, another aromatic compound, also has a significantly higher octane rating than isooctane. According to BS VI specifications (Bharat Stage VI), the octane rating of normal petrol is fixed at 91.

Now, let's discuss the calorific value. For fuels, the calorific value is a very important property. Calorific value is the quantity of heat released per unit quantity of fuel when it is burned completely with oxygen and the products of combustion return to the ambient temperature. This is the general definition of calorific value. Calorific value can be classified into two types: one is gross calorific value, which is also known as higher heating value or higher calorific value.

Another one is the net calorific value, which is the lower heating value or lower calorific value. Both of these calorific values can be determined at constant volume and constant pressure. For solid and liquid fuels, their calorific value is determined at constant volume, while for gaseous fuel, the calorific value is determined at constant pressure. Now, gross calorific value at constant volume can be defined as follows: It is the heat liberated by burning a definite quantity of fuel at constant volume in oxygen saturated with water vapor. The original material and the final product of combustion are at the reference temperature of 25 degrees Celsius, and the water produced by burning the fuel is in a liquid state.

On the other hand, the net calorific value at constant volume is the same, except the water produced due to the burning of fuel will be in the vapor state. So, you can understand that the gross calorific value is higher than the net calorific value by the amount of heat that is released during the condensation of water vapor. This heat of condensation is added to the gross calorific value along with the heating value of the fuel. That is why the gross calorific value is referred to as the higher heating value or higher calorific value, while the net calorific value is referred to as the lower calorific value or lower heating value. This chart shows the calorific value of some petroleum fuels. Natural gas has a calorific value ranging from 42 to 55 megajoules per kilogram.

LPG liquefied petroleum gas is 46 to 51, petrol or gasoline shows 44 to 46 diesel fuel is 42 to 46 megajoules per kg. All of these have very high calorific value and are very good fuel. Now, coming to the discussion on the induction period of gasoline. The induction period of gasoline is that it is the time up to which the gasoline can be stored without the formation of any gum. So, this test is required for the determination of the oxidation stability of gasoline under accelerated oxidation conditions.

We know that gasoline is stored in the floating head roof storage tanks. So, gasoline may always be in contact with the oxygen in the air. It is open some part of the gasoline surface is open to the atmosphere. So, gasoline is always prone to oxidation by aerial oxygen. Prolonged storage of gasoline may form sticky gum in it and the gum will destroy some valuable components of the gasoline and this causes many disadvantages and difficulties during storage as well as transportation and in the gasoline engine.

So, this induction period gives us a measure of how long we can store gasoline without the formation of gum. It provides information about the storage stability of gasoline. This test is necessary for determining the oxidation stability of gasoline under accelerated oxidation conditions. The longer the induction period, the better the storage stability of the fuel. Typically, the standard storage time is observed to be between 240 to 480 minutes. An induction period of 360 minutes under laboratory conditions ensures the storage stability of at least 6 months. Now, how is the induction period of gasoline measured? A measured quantity of gasoline is taken in a steel pressurized bomb where oxygen is introduced at a pressure of around 6 bar, and the temperature is maintained at around 100 degrees Celsius.

At this condition, the gasoline pressure increases inside the bomb, and the increase in pressure is continuously recorded. Eventually, a point will be reached where there is a very sharp rise in the gasoline pressure within the bomb, and that time is noted. This time is referred to as the induction period of gasoline. Now, let's discuss the Water Separometer Index (WSIM). This parameter measures the water separation characteristics of fuels. Typically, aviation fuels are the ones that need to check their Water Separometer Index, especially at high altitudes where moisture can come into contact with the fuel. Under such conditions, moisture can form an emulsion with the fuel, and this emulsion is often supported by surfactant additives present in aviation fuel.

Aviation fuel is enhanced by adding various types of additives, and surfactants are among them. Surfactants help emulsify water with the oil, which can degrade the quality of the oil. WSIM is a measure of fuel cleanliness in relation to its ability to be free from surfactant materials. This test method is used to evaluate the ability of aviation turbine fuels to release entrained or emulsified water when passed through fiberglass coalescing material. There is equipment that includes fiberglass coalescing material through which the fuel is passed, and this material helps separate the emulsified water from the fuel.

If water coalesces easily, then aviation turbine fuel has a higher WSIM value. A higher WSIM rating indicates that the fuel is cleaner in relation to surfactant materials. Whether or not it contains surfactant material, a higher WSIM value suggests that the fuel performs better in terms of cleanliness, even in the presence of water. Now, let's discuss the use of lead in gasoline. As we've already discussed, tetraethyl lead is added to gasoline to improve its octane number as an antiknock agent. Although tetraethyl lead is added to gasoline in a very low quantity, approximately 3 milliliters per barrel of oil, it still poses many harmful effects. Lead is a toxic metal that interferes with anti-pollution devices and contributes to lead poisoning.

If gasoline contains lead, such as tetraethyl lead or alkyl lead compounds, when it is burned, it forms lead particulates in the exhaust gas along with sulfur dioxide and nitrogen dioxide, which are byproducts of fuel combustion. In the exhaust system of many cars, a catalytic converter is placed to convert these sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) emissions. The catalytic converter ensures that the exhaust gas emitted through the exhaust line is cleaner and meets clean air specifications. However, if lead particulates are present in the exhaust, they can passivate or deactivate the catalyst within the catalytic converter, leading to reduced exhaust quality.

Lead is still used in aviation gasoline for some piston engine propeller aircraft. Nevertheless, efforts are being made to lower and eventually remove lead from this type of fuel as well. Even though a small quantity of lead alkyl compounds can effectively improve or enhance the octane number, there are now several other compounds, such as oxygenated compounds, that can also boost the octane number. These alternative compounds are being explored. One of the primary international standard test methods for measuring lead in gasoline is X-ray spectroscopy, specifically X-ray fluorescence (XRF). X-ray fluorescence spectroscopy is employed to determine the lead content in gasoline.

In fact, X-ray fluorescence (XRF) is used to measure the metal content in any liquid or solid. This method is also used to determine the lead content in gasoline. It's an ASTM method and covers the determination of total lead content in gasoline within the concentration range of 0.01 gram to 0.1 gram of lead per US gallon, which is equivalent to 2.5 milligrams to 25 milligrams per liter. This method spans a range from low to very high lead content.

Now, let's discuss color, which is an important property of petroleum fuels because it provides an identity to the petroleum fuel. Color also indicates the degree of refining of the products. The more refined the product, the clearer and more transparent it appears, often having a very light yellowish hue. However, some petroleum products are intentionally mixed with dyes to give them a distinct identity. Various test methods are used to measure the color of petroleum products, and they are associated with their main components and application ranges. The chart below displays the equipment names, color scales, and the products to which they are applied. One such equipment is the Saybolt Chromometer, which measures color on a scale ranging from plus 30 to -16. This chronometer is used to determine the color of white and clear petroleum products. There's also the ASTM colorimeter, specifically designed to determine color.

The ASTM colorimeter has a scale from 0 to 8, and it is used to determine the color of heavy petroleum products, such as lubricating oil, which are somewhat thicker in consistency. The color of dyed aviation gasoline is determined using a color comparator, which consists of permanent color glass discs. This equipment is employed to ascertain the color of dyed aviation gasoline, giving it a distinct identity from regular gasoline. The Lovibond Tintometer is a widely used piece of equipment that determines the color of many petroleum products. It includes color shade standards with different ratings for red, yellow, blue, and neutral tints. These standards are used for color determination in all petroleum products except for black oils and bitumens.

These are the references. Thank you for your attention.