Energy Conversion Technologies (Biomass and Coal)

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Lecture 10

Liquid fuels (Part I)

Good morning everyone.

Welcome to part 1 of lecture 2 under the module 2. In this lecture we will discuss about the liquid fuel and its properties.

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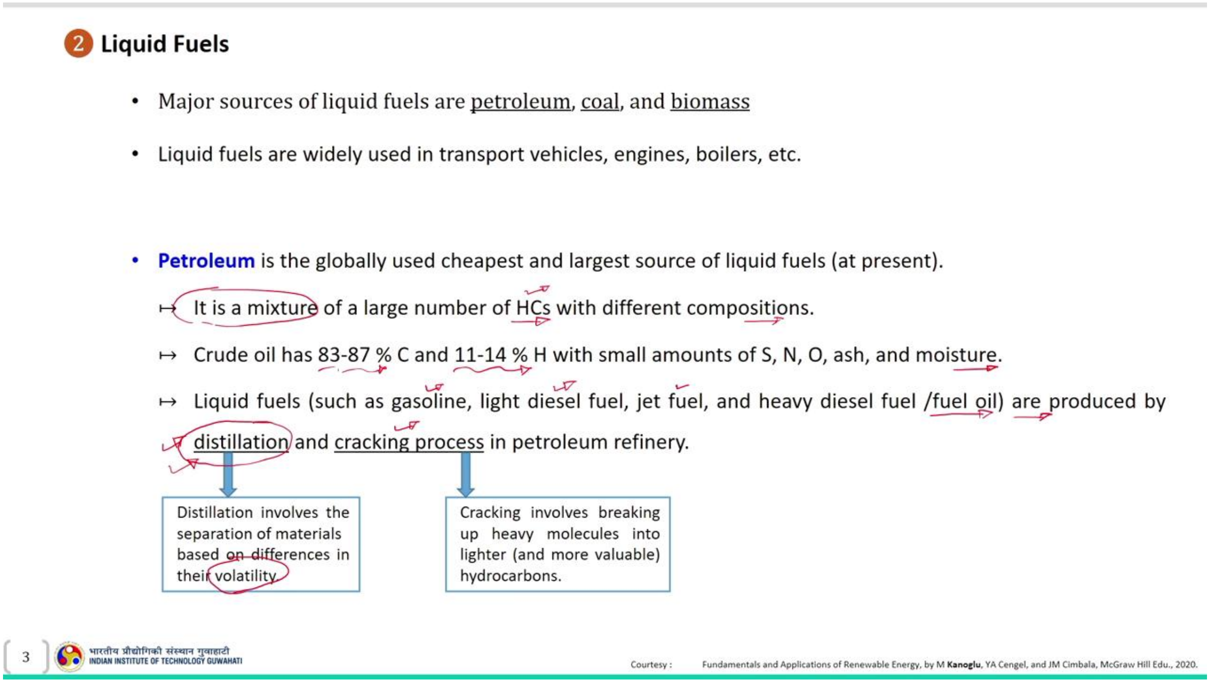

Major sources of liquid fuel are petroleum, coal and biomass and the liquid fuel derived from these sources is widely used in transport vehicle, engines and boilers. Apart from that these liquid fuels are widely used in various other applications. Among these sources petroleum is the globally used cheapest and largest source of liquid fuel at present.

And this petroleum liquid fuel it is a mixture of large number of hydrocarbons with even different composition. And the hydrocarbons in the petroleum product are mostly alkanes, naphthenes and various aromatic hydrocarbons. Crude oil it has around 83 to 87% of carbon and 11 to 14% of hydrogen with small amount of sulfur, nitrogen, oxygen, ash and moisture. These liquid fuels from the petroleum source are produced by distillation and cracking process in petroleum refinery.

And these liquid fuels include gasoline, light diesel fuel, jet fuel, heavy diesel fuel which is also known as fuel oil. So, this distillation involves the separation of materials based on differences in their volatility. And it is one of the most common operations in the petroleum refinery. Apart from that cracking process involves breaking up of heavy hydrocarbon molecule into lighter hydrocarbons. And this is also one of the most common operations in the petroleum refinery. While coal and oil shale are being processed in some countries to produce substitute fuel.

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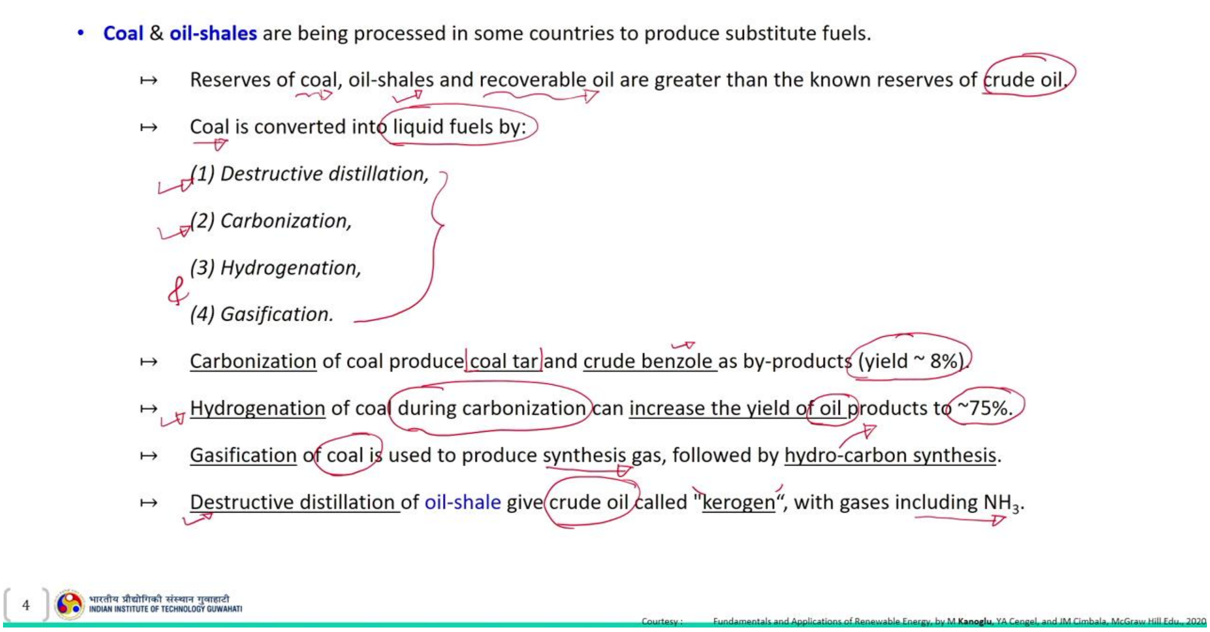

Reserves of coal oil shells and recoverable oil these are greater than the known results of crude oil. And the coal is converted into liquid fuel by various conversion techniques including destructive distillation carbonization, hydrogenation and gasification. So, here the carbonization of the coal it produces mainly coal tar as a product along with the crude benzol as a byproduct. And it is around 8% in the product stream of the carbonization process. And hydrogenation of coal during carbonization it eventually results in increase in the yield of oil and it goes up to even 75%.

And the gasification of coal which is a very popular method to produce synthesis gas and this produced synthesis gas can further be converted into a hydrocarbon fuel using the gas to liquid process. The destructive distillation of oil-shell gives crude oil which is also known as a "kerogen" with gases including ammonia as a byproduct. These are basically some conversion techniques to convert coal into liquid fuels.

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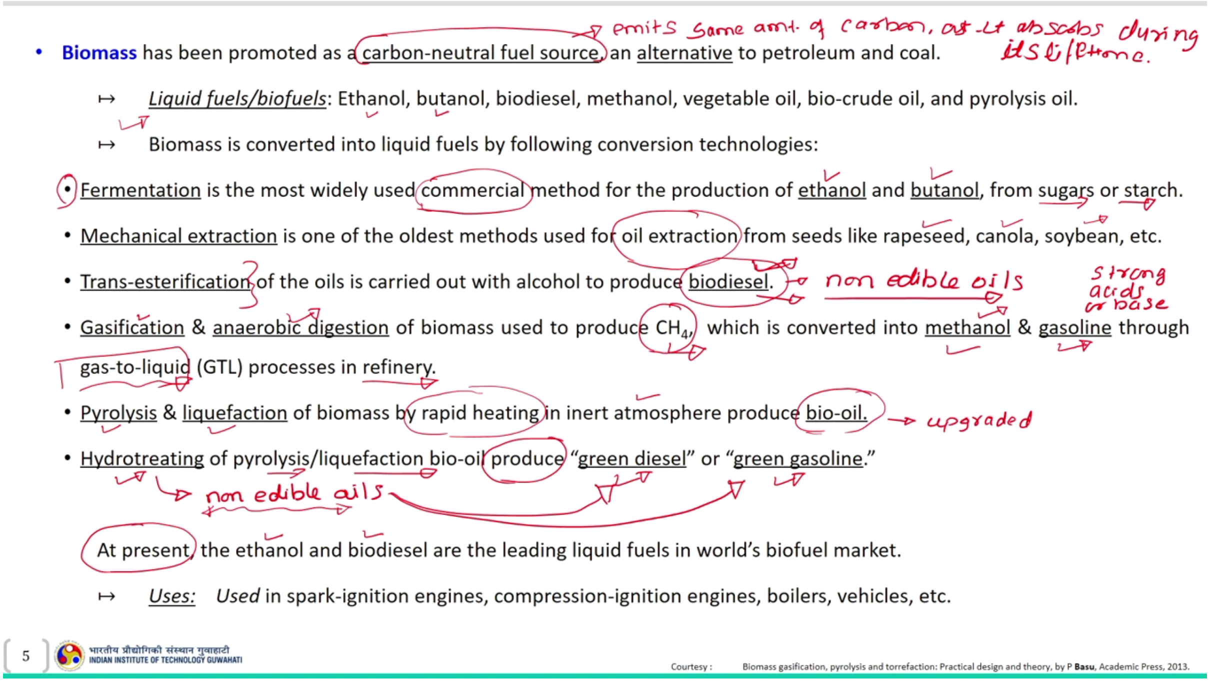

Apart from this petroleum sources that is petroleum crude oil and coal, biomass is considered carbon neutral fuel source. Because it emits same amount of carbon when combusted as it absorbs during its lifetime.

If biomass is not utilized as a fuel source, it still emits the same amount of carbon if it decomposes naturally. However, a lot depends on the fuel source, the processing involved and the method of biomass utilization, process to produce the liquid fuel which is widely known as biofuels such as ethanol, butanol, biodiesel, methanol, vegetable oil, bio crude oil and pyrolysis oil. The biomass is converted into these liquid fuels by various conversion technologies and some of these technologies are listed here. Fermentation is already a well established technology for the conversion of sugars into ethanol. Similarly, the mechanical extraction is one of the oldest methods used for the oil extraction from oil seeds like rapeseed, canola, soybean and many more.

Biodiesel is one of the most widely used liquid fuels for energy generation and it is mainly produced from non edible. Similarly, the non-edible oil seeds are used in the mechanical extraction process to extract the oil. And this processed oil is used for the synthesis of biodiesel using transesterification process in which mainly the triglyceride component of the oil reacts with alcohol in presence of strong acids or base as catalyst to convert it into methyl ester of requisite standard. Apart from that, gasification and anaerobic digestion of biomass is used to produce methane which further converts into a methanol and gasoline through gas to liquid process in the refinery. So, these are also two popular technologies to convert biomass into methane.

And further the produced methane is converted into liquid fuel in the form of methanol and gasoline through this gas to liquid conversion process. Apart from that the paralysis and liquefaction of the biomass by rapid heating in the inner atmosphere produces bio oil as a product. And this produced bio oil can further be upgraded using the conversion technology that is called as a hydrotreating technology. So, in this process the pyrolysis or liquefaction oil, so as we just discussed before, can be converted into a green diesel or green gasoline. Apart from that the hydrotreating of non edible oils can also produce green diesel and green gasoline as a product.

And this is also one of the most popular and upcoming technology to produce green diesel and green gasoline. So, at present Ethanol and biodiesel are the leading liquid fuels in the world's biofuel market and these are used in spark ignition engines, compression ignition engines, boilers and vehicles.

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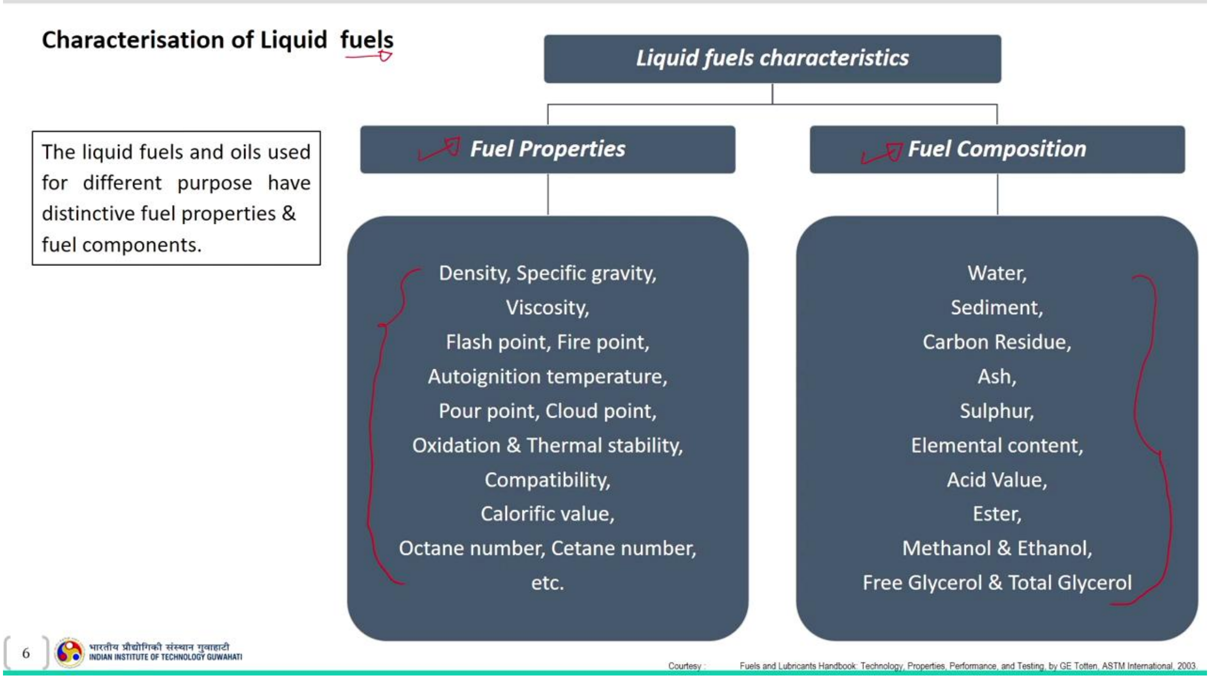

Since these liquid fuels are derived from various different source materials and also various conversion or processing technologies are used to convert this source material into a liquid fuel, hence, their characterization is essential to know their fuel properties and fuel composition. So, here we will discuss about the fuel properties and composition of the specific liquid fuel derived from the specific source material.

So, the characterization of the liquid fuels involves estimation of the fuel properties and the fuel composition and the list which is given here is a comprehensive list of fuel properties which are majorly used to estimate the properties of the liquid fuel. And this particular comprehensive list indicates the estimation of composition of the liquid fuels.

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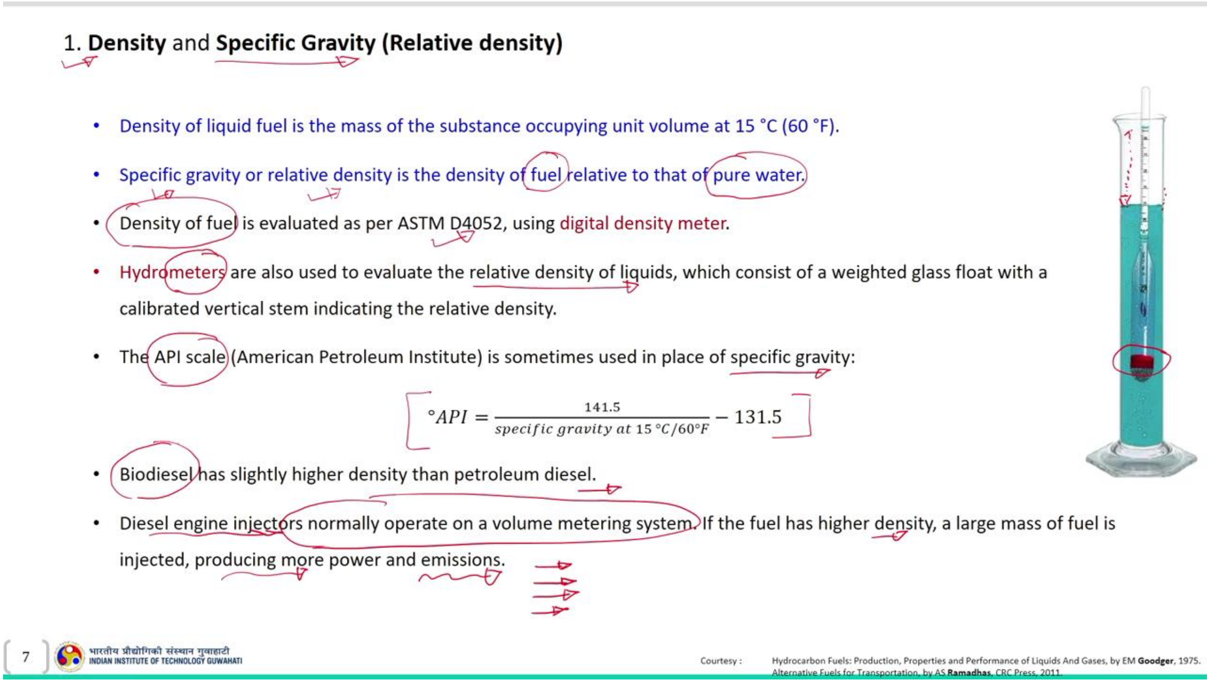

So, let us discuss about the fuel properties first. So let us begin with the density and specific gravity. Density of a substance or liquid fuel is the mass of the substance occupying a unit volume at 15 degree Celsius. Similarly, specific gravity or relative density, it is the density of fuel which is relative to that of the pure water and density of the fuel is evaluated using the standard ASTM method using digital density meter.

However, hydrometers are also used to evaluate the relative density of a liquid which consists of a weighted glass float with a calibrated vertical step indicating the relative density. The API scale is sometimes used in place of the specific gravity and it can be estimated using this following expression. Compared to the petroleum diesel, the biodiesel has slightly higher density and the diesel engine injectors which are normally operate on a volumetric system.

If the fuel has higher density, then a large mass of fuel is injected and that eventually results in producing more power, but also it emits more pollutant. That is also one of the disadvantages. So, this density value should limit to its standard value so that it can be used as a fuel in the diesel engine.

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2. **Viscosity**

- The weak van der Waals-type forces between molecules provide cohesion to a body of liquid, and hence a resistance to internal displacement and flow. This resistance is termed the **viscosity**.
- There are two kinds of viscosity commonly reported, kinematic and dynamic.
- **Dynamic viscosity (η)** of a liquid may be defined as the tangential force on unit area of either of two parallel planes at unit distance apart when the space between the planes is filled with the liquid sample, and one of the planes moves with unit velocity in its own plane relative to the other.

Units of dynamic viscosity:

$$\eta = \frac{Force}{Area \times (Velocity/Length)} = \frac{N}{m^2 \times \left(\frac{m}{s} \times \frac{1}{m}\right)} = Ns/m^2 = kg/m \cdot s$$

In metric system, the unit of dynamic viscosity is the g/cm s, or poise (P).

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Courtesy : Hydrocarbon Fuels: Production, Properties and Performance of Liquids And Gases, by EM **Goodger**, 1975. Alternative Fuels for Transportation, by AS **Ramadhas**, CRC Press, 2011.

The next in the properties is the viscosity. The weak van der Waals type forces between molecules provide a cohesion to a body of a liquid and hence a resistance to internal displacement and flow. And this resistance is termed as the viscosity. There are two kinds of viscosity commonly used that is kinematic viscosity and the dynamic viscosity.

The dynamic viscosity of a liquid, it may be defined as the tangential force on unit area of either of the two parallel planes that are under consideration at unit distance apart when a space between these two plane is filled with the liquid sample and one of the planes moves with a unit velocity in its own plane relative to the other.

And the following equation can be used to estimate the dynamic viscosity of a given fuel. And the unit of dynamic viscosity is Newton second per meter square and it also represented in the form of kilogram per meter second. While in metric system the unit of dynamic viscosity is gram per centimeter second or poise.

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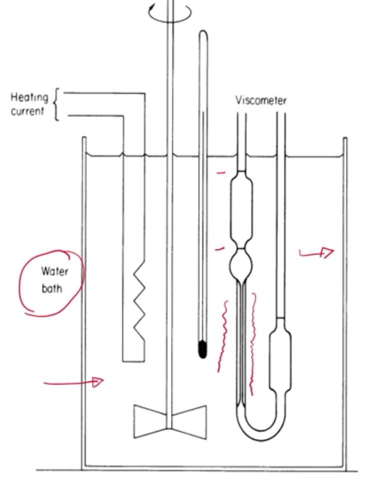
- **Kinematic viscosity (ν)** of a liquid may be defined as the quotient of the dynamic viscosity and the density of the liquid.

Units of kinematic viscosity

$$\nu = \frac{\eta}{Density} = \frac{kg/ms}{kg/m^3} = m^2/s$$

In metric system, the unit of kinematic viscosity is the cm^2/s, or stokes (St).

U-tube viscometer with capillary tube



It is measured using the ASTM Standard D445, employing a glass U-tube viscometer with a capillary tube built into one leg.

It is determined by measuring the time taken for a fixed volume of fuel to flow a known distance under gravity through the capillary tube viscometer at controlled temperature.

Courtesy : Hydrocarbon Fuels: Production, Properties and Performance of Liquids And Gases, by EM **Goodger**, 1975. Alternative Fuels for Transportation, by AS **Ramadhas**, CRC Press, 2011.

Similarly, the kinematic viscosity of a liquid it may be defined as the quotient of dynamic viscosity and the density of a liquid. And it is the relationship between the viscous and the inertial forces in the fluid.

And the unit of kinematic viscosity is meter square per second and in metric system the unit of kinematic viscosity is centimeter square per second or it also represented in the form of Stokes. And it is measured using this standard ASTM technique employing glass U tube viscometer with a capillary tube built into one leg.

And the viscosity of a given fuel is measured by using this U tube viscometer, where the time taken for a fixed volume of fuel to flow unknown distance under gravity through the capillary tube viscometer at a controlled temperature. And this temperature here is controlled using a water bath. And even intermittently the stirring is provided here in the water bath to maintain the controlled temperature. This is one of the most widely used apparatus for the estimation of the kinetic viscosity of a given fuel.

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- Viscosity of fuel increases with chain length (number of carbon atoms). This holds also for the alcohol moiety because the viscosity of ethyl esters is slightly higher than that of methyl esters.
- Viscosity of fuel increases with increasing degree of saturation. Factors such as double-bond configuration influence viscosity; cis double-bond configuration giving a lower viscosity than trans.
- Higher viscosity of fuel leads to:
  - ↦ Poor atomization (fuel droplet size) and spray characteristics,
  - ↦ Incomplete combustion,
  - ↦ Increased carbon deposits,
  - ↦ Higher pumping power.

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Viscosity of the fuel, it increases with the chain length and this holds for the alcohol moiety. Because the viscosity of ethyl ester is slightly higher than that of the methyl ester. And viscosity of the fuel it also increases with increasing the degree of saturation. The factors such as double bond configuration influence the viscosity that is cis bond configuration giving a lower viscosity than trans. And this is mainly for the biodiesel fuel because biodiesel is a mixture of cis and trans fatty acids.

Higher viscosity of the fuel has certain issues because it leads to poor atomization and spray characteristics, incomplete combustion, increased carbon deposits and higher pumping power. Hence, it is always recommended to restrict the viscosity of a given fuel to its standard limits.

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3. **Flash Point, Fire Point** and **Auto-ignition Temperature**

Flash point of a liquid fuel is defined as the lowest temperature (at 101.3 kPa pressure) at which application of the ignition source causes the vapor of the fuel to ignite.

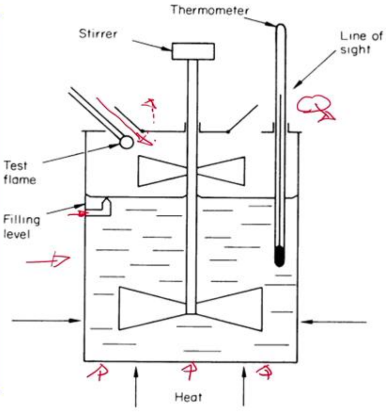
- There are several methods for Flash point test based on apparatus, e.g. ASTM D56, ASTM D93, etc.

ASTM D93 test method (by Pensky-Martens closed cup apparatus):

↦ Specified volume of fuel sample filled into a brass test cup of specified dimensions.

↦ Cup is closed and heated while stirring the fuel at specified rpm.

↦ An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring until a flash is detected.



Closed cup flash-point apparatus

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Courtesy : Hydrocarbon Fuels: Production, Properties and Performance of Liquids And Gases, by EM **Goodger**, 1975. Alternative Fuels for Transportation, by AS **Ramadhas**, CRC Press, 2011.

And next in the list is the flash point, fire point and the ignition temperature. Flash point of a liquid fuel is defined as the lowest temperature at which the application of ignition source causes the vapor of fuel to ignite. There are several methods used for the flash point test based on the apparatus and this includes ASTM D56 method and ASTM D93 method.

So, the ASTM D93 test method by Penske-Martins close curve apparatus is shown here in the schematic. So, in this test a specified volume of a fill sample is filled into brass test cup of a specified dimension. And if you see here the filling level is also shown here in the schematic, it should be filled up to this particular level. And then the cup is closed and heated while stirring the fuel at specified rpm.

An ignition source is directed into the test cup at regular interval with simultaneous interruption of the stirring until the flash is detected here in this particular zone. And the corresponding temperature recorded here in the thermometer is considered as the flashpoint of the given fuel.

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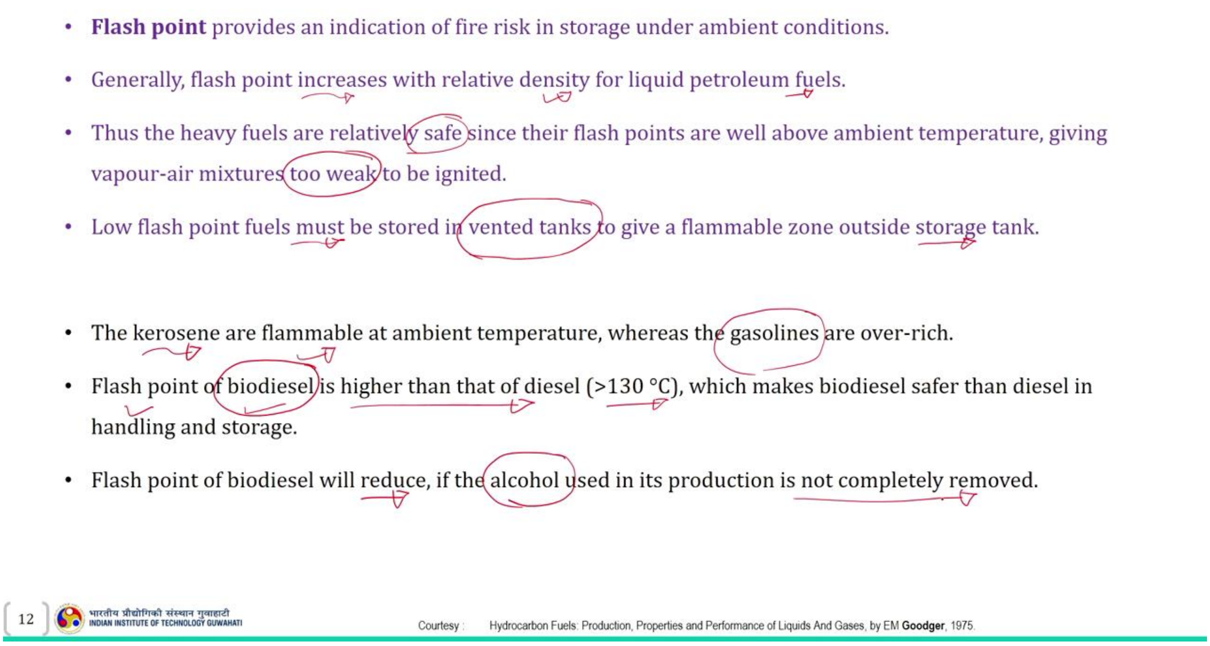

The purpose of estimation of the flash point is the flash point provides an indication of fire risk at storage under ambient condition. In general, flash point increases with relative density for liquid petroleum fuels. Thus, the heavy fuels are relatively safe since their flash points are well above the ambient temperature giving vapor air mixture too weak to be ignited. And low flash point fuels, it must be stored in vented tanks to give a flammable zone outside the storage tank.

The kerogens are flammable at ambient temperature whereas the gasolines are over rich. Similarly, the flash point of the biodiesel it is higher than that of the diesel even greater than 130 °C which makes biodiesel safer than diesel in handling and storage. And this flash point of the biodiesel will reduce if the alcohol used during the transesterification process is not completely removed even it will reduce the flash point of biodiesel.

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Fire point is the lowest temperature (at 101.3 kPa), at which the application of an ignition source causes the vapors of a fuel being tested to ignite and continue to burn for 5 s under the specified conditions of the test.

↦ Fire point of fuel is little higher than its flash point.

↦ Fire point of liquid fuels is determined by ASTM D92 (by Cleveland open cup apparatus).

Autoignition temperature is the temperature at which the fuel will ignite spontaneously in contact with air, in the absence of sparks or flame.

↦ Autoignition temperature is determined by Test Method ASTM E659 and ASTM D659.

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Courtesy : Hydrocarbon Fuels: Production, Properties and Performance of Liquids And Gases, by EM Goodger, 1975.

Similarly the fire point is the lowest temperature at which application of an ignition source causes the vapour of liquid fuel being tested to ignite and burn continuously for 5 seconds under the prescribed condition of the test. And this fire point of the fuel is slightly higher than its flash point. And the fire point of the liquid fuel can be estimated using this standard ASTM technique by Cleveland open cup apparatus.

Similarly, the ignition temperature is the temperature at which the fuel will ignite spontaneously in contact with air even in absence of sparks or flame. And this auto ignition temperature it can also be estimated using the standard ASTM technique mentioned here. Hence the estimation of flash point, fire point and at ignition temperature is essential. Because these properties provide the indication of fire risk in storage even at ambient condition.

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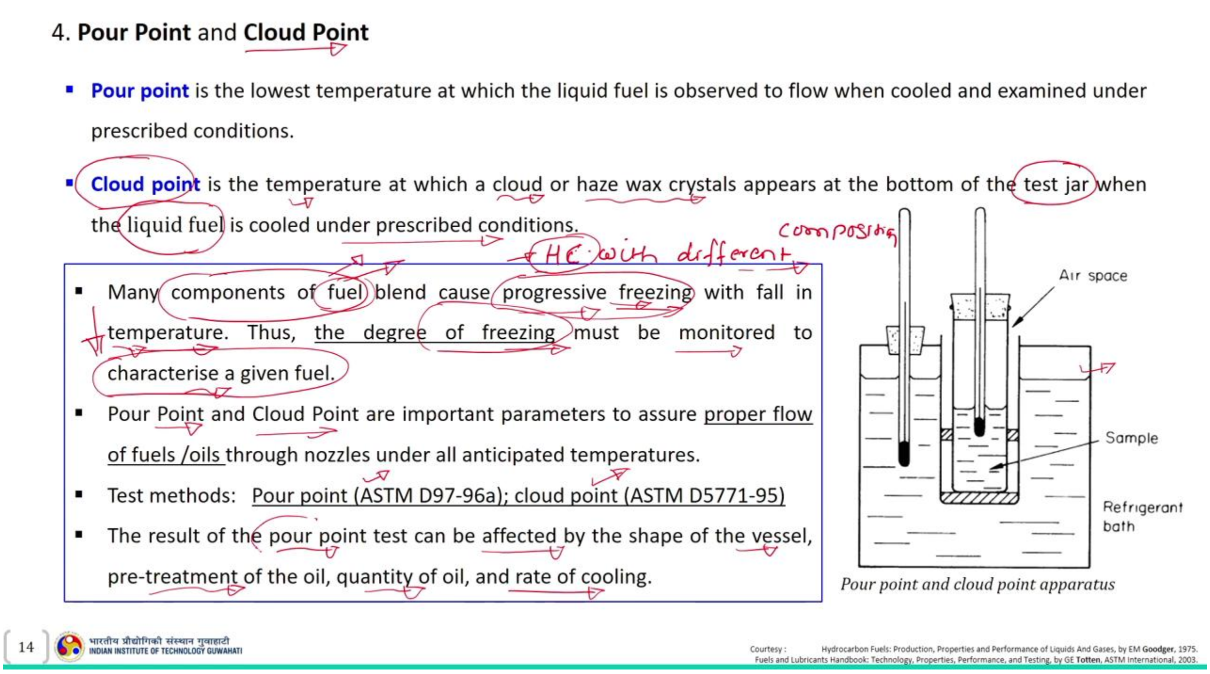

So, the another important property for the liquid fuel is the pour point and the cloud point. Pour point is the lowest temperature at which the liquid fuel is observed to flow when cooled and examined under the prescribed condition. Similarly, the cloud point is the temperature at which a cloud or wax crystals appears at the bottom of test jar when the sample is cooled under prescribed condition.

So, once we observe such cloud or hazy waxy crystals at the bottom of the test jar for a given liquid sample then with the help of the proper setup we can estimate the cloud point of a given sample. Many components of fuel blend causes progressive freezing with fall in the temperature. If you recollect just few slides back, we discussed about the petroleum derived liquid fuel and the biomass base derived liquid fuel. And this liquid fuel is a mixture of large hydrocarbons with different composition.

So, because of this vast difference in their composition and because of this various component which are present in this liquid fuel. So, some of the component of the fuel blend may cause progressive freezing with a decrease in the temperature. Thus, the degree of freezing must be monitored to characterize the given liquid fuel.

Pour point and cloud point are the important parameter to assure proper flow of fuels through nozzles under all anticipated temperature. And these ASTM techniques are used to measure the power point and the cloud point of a given fuel. And this particular schematic represents the setup which is used to measure the cloud point and power point of the given fuel. And the result of power point test can be affected by the shape of the vessel which is used during this test method.

Pre-treatment of the oil, if the given oil sample is pre-treated before the test then there might be some change in the pour point estimation values, quantity of the oil used during the estimation of the pour point and the cloud point and the rate of cooling. So, these factors even affect the result of power point and cloud point test.

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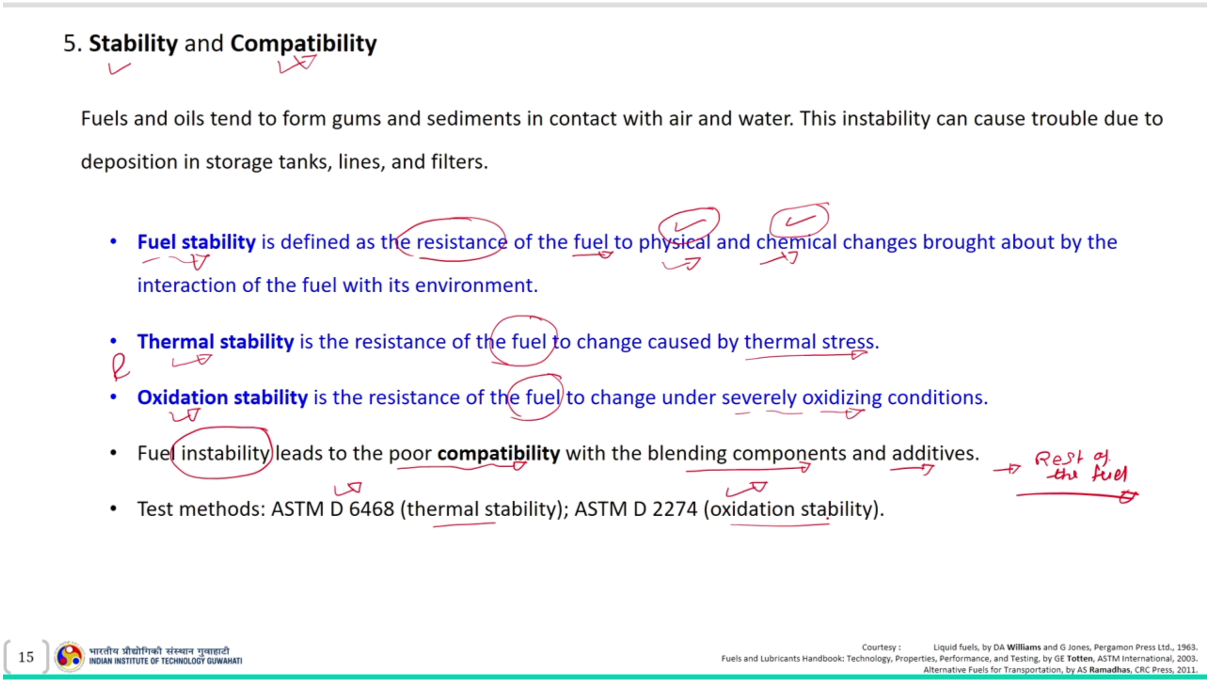

So, another important property of the liquid fuel is stability and compatibility. Fuels and oils tend to form gums and sediments in contact with air and water. This instability can cause trouble due to deposition in tanks, lines and filters. Fuel stability is defined as the resistance of the fuel to physical and chemical changes which are brought about by the interaction of the fuel with its environment.

For example, in case of biodiesel, if it remains exposed to the environment, then it undergoes the autoxidation reaction, which eventually results in the change in the chemical and the physical properties of the produced fuel and which ultimately hampers its fuel properties. Thermal stability, it is the resistance of fuel to change caused by the thermal stress. And the oxidation stability is the resistance of the fuel to change under severely oxidizing condition.

So, as I just mentioned before if the biodiesel is exposed for a long time into the environment then it undergoes the autoxidation reaction where it undergoes the physical and the chemical changes which ultimately hampers its fuel properties that is because of the oxidation of certain components which are present in the biodiesel. As we know the biodiesel it is a mixture of saturated and unsaturated fatty acids.

So, basically the unsaturated fatty acids are prone to the auto-oxidation if it remains exposed into the environment for a longer time. So, this fuel instability it leads to the poor compatibility with blending components and additives. That means if the prepared fuel get affected by any of this stability then it may result into formation of the some sediments and the gums. So, which eventually results in the separation of certain component of fuel from rest of the fuel as a result it will get separated from the blending components or the additives.

And that is essentially needed to be avoided in case of the liquid fuels. So, these particular standard methods are used to estimate the thermal stability and the oxidation stability of the liquid fuel.

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- E.g.:
  - ↦ Biodiesel ages more quickly than diesel due to chemical structure of methyl esters present in biodiesel.
  - ↦ Saturated methyl esters in biodiesel increase its cloud point and cetane number and improve its stability.
  - ↦ The unsaturated fatty acids reduce cloud point and cetane number and reduce its stability also.
- Additives can be used to improve stability and also to inhibit rust formation.

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Courtesy : Liquid fuels, by DA **Williams** and G Jones, Pergamon Press Ltd., 1963.
Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, by GE **Totten**, ASTM International, 2003.
Alternative Fuels for Transportation, by AS **Ramadhas**, CRC Press, 2011.

As just discussed before, the biodiesel, it ages more quickly than the diesel due to the chemical structure of the methyl stress present in the biodiesel. So, that is what I have just discussed one slide before. If the biodiesel is exposed to environmental condition for a longer time, then because of the autoxidation reaction, some physical and chemical changes may occur in the biodiesel. And that is mainly because of the chemical structure of the biodiesel, as it mostly consists of the ester molecules which are prone to the autoxidation.

And that eventually results into the change in the chemical and the physical properties of the prepared biodiesel and which eventually hampers its fuel properties as well. The saturated methyl stress in biodiesel increases its cloud point and cetane number and also improves its stability. But the unsaturated fatty acids reduce the cloud point and cetane number and also reduce its stability and for that reason the additives are used to improve the stability of a fuel and also to inhibit the rust formation during its use.

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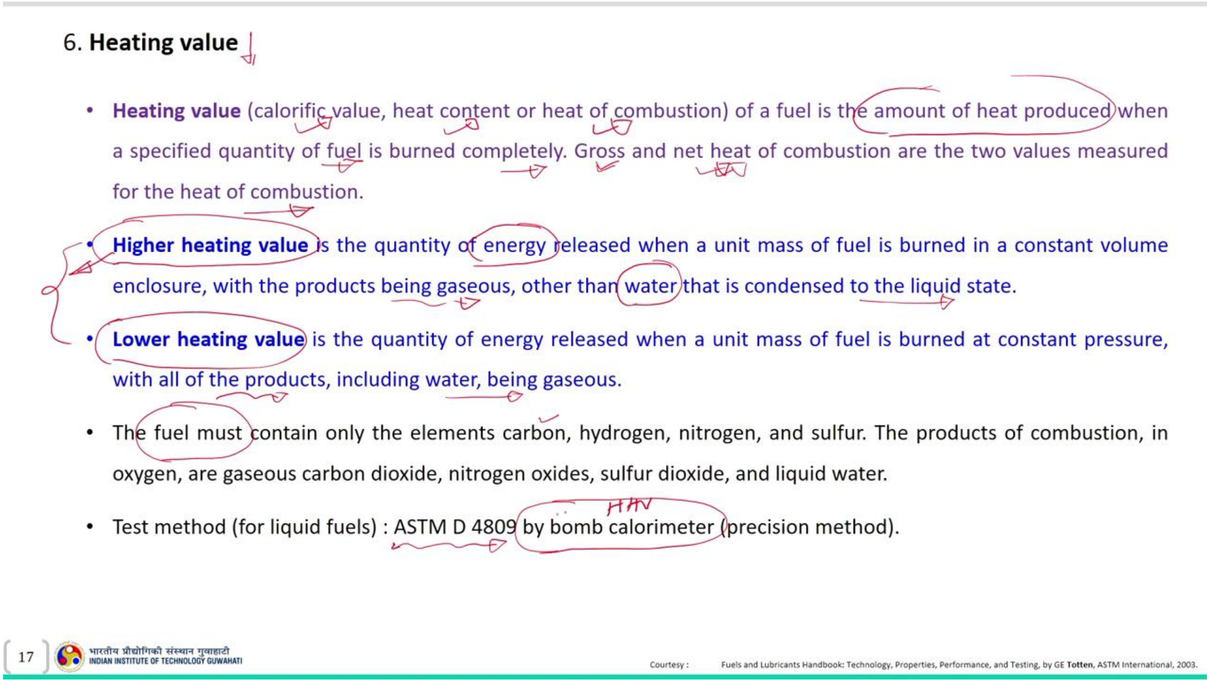

The another important property of the liquid fuel is the heating value. The heating value which is also known as a calorific value. The heat content or heat of combustion of a fuel is the amount of heat produced when a specified quantity of fuel is burned completely. The gross and the net heat of combustion are the two values major for the heat of combustion and these are also known as the gross calorific value and the net calorific value.

The higher heating value is the quantity of energy released when a unit mass of fuel is burned in a constant volume enclosure with products being gaseous other than the water that is condensed to the liquid state. And this higher heating value of a given liquid fuel can be estimated using a known apparatus that is called as a bomb calorimeter. Similarly, the lower heating value It is the quantity of energy released when the unit mass of a fuel is burned at a constant pressure with all the products including water being gaseous.

So, this is the major difference between these two values that is higher heating value and the lower heating value. And this concept of higher heating value as well as the lower heating value also we discussed in one of the lecture in module 1. The fuel must contain only elements like carbon, hydrogen, nitrogen and sulphur. And the products of this combustion in oxygen are gaseous carbon dioxide, nitrogen oxides, sulphur dioxide and liquid water. And this is the standard ASTM technique which is used for the estimation of the heating value of a given sample. And mostly we estimate the higher heating value of a given fuel using this bomb calorimeter.

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Relation between HHV and LHV:

$$HHV = LHV + 0.2122H \quad \text{(at 25 °C)}$$

Where, HHV = higher heating value at constant volume, MJ/kg

LHV = lower heating value at constant pressure, MJ/kg

H = mass % hydrogen in the sample

HHV or LHV can also be calculated as:

$$HHV = LHV + Q_{latent}$$

$$Q_{latent} = m_{H_2O}\, h_{fg}$$

Where, Q_{latent} = latent heat of water, MJ/kg

m_{H2O} = mass of water formed per unit mass of fuel burned, kg_{water}/kg_{fuel}

h_{fg} = enthalpy of vaporization of water at 25°, MJ/kg

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Courtesy : Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, by GE **Totten**, ASTM International, 2003.

And once we know the higher heating value of a given fuel, then we can easily estimate the lower heating value of the given fuel using this relation. So, here the H is nothing but the mass percentage of hydrogen in the sample. So, apart from this relation even the lower heating value of given sample can be estimated using this another relation.

So, in this relation we need to know this latent heat of water which can be estimated by this equation. And once we know the Q latent and the HHV, then we can easily estimate the lower heating value of a given fuel.

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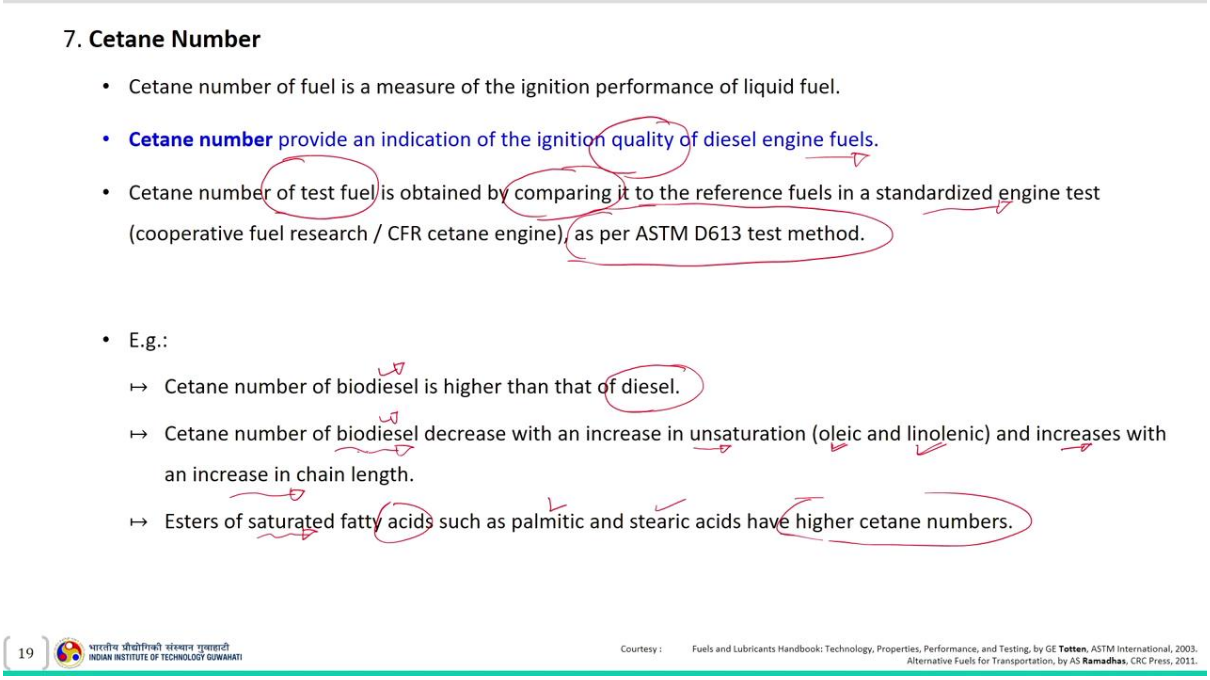

And next in the list is the cetane number, which is also one of the important properties of a liquid fuel. Because cetane number of a fuel it is a measure of the ignition performance of a liquid fuel. It provides an indication of the ignition quality of a diesel engine fuels. And the cetane number of a test fuel can be obtained by comparing it to the reference fuel in the standardized engine test.

And this can be obtained using the standard ASTM method. And this certain number of the biodiesel is higher than that of the petroleum diesel. If the percentage of oleic and linolenic in the biodiesel it increases then eventually it decreases the cetane number of the biodiesel and increases with increase in the chain length.

Since the biodiesel it is a mixture of the saturated and the unsaturated fatty acid. So, the traces of the saturated fatty acids, such as palmitic and the steric acids have higher cetane numbers. So, proper mixture composition of unsaturated fatty acid and saturated fatty acid need to be maintained in the biodiesel sample during its preparation, so as to obtain an optimum cetane number.

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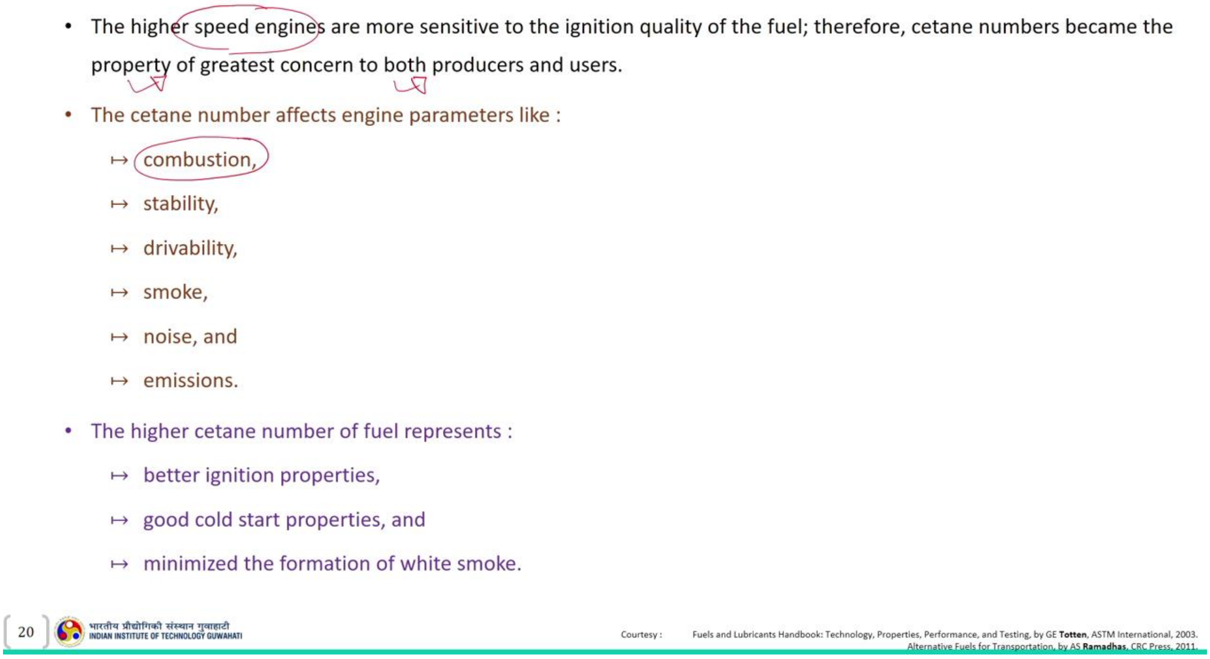

The high speed engines are more sensitive to the ignition quality of the fuel. And therefore, the cetane number became the property of greatest concern to both the user as well as the producers. And the cetane number it affects the engine parameters such as combustion, stability, drivability, smoke, noise and the emission.

The higher certain number of the fuel represents the better ignition properties, good cold flow properties and also helps to minimize the formation of the white smoke. So, these are the advantages of having the higher certain number of the liquid fuel.

So, this comprises the fuel properties of a given liquid fuel. So, with this we will end our lecture here. So, in the next lecture we will discuss about the fuel component characteristics.

Thank you.