Energy Conversion Technologies (Biomass and Coal)

Prof. Vaibhav V. Goud

Department of Chemical Engineering

Indian Institute of Technology, Guwahati

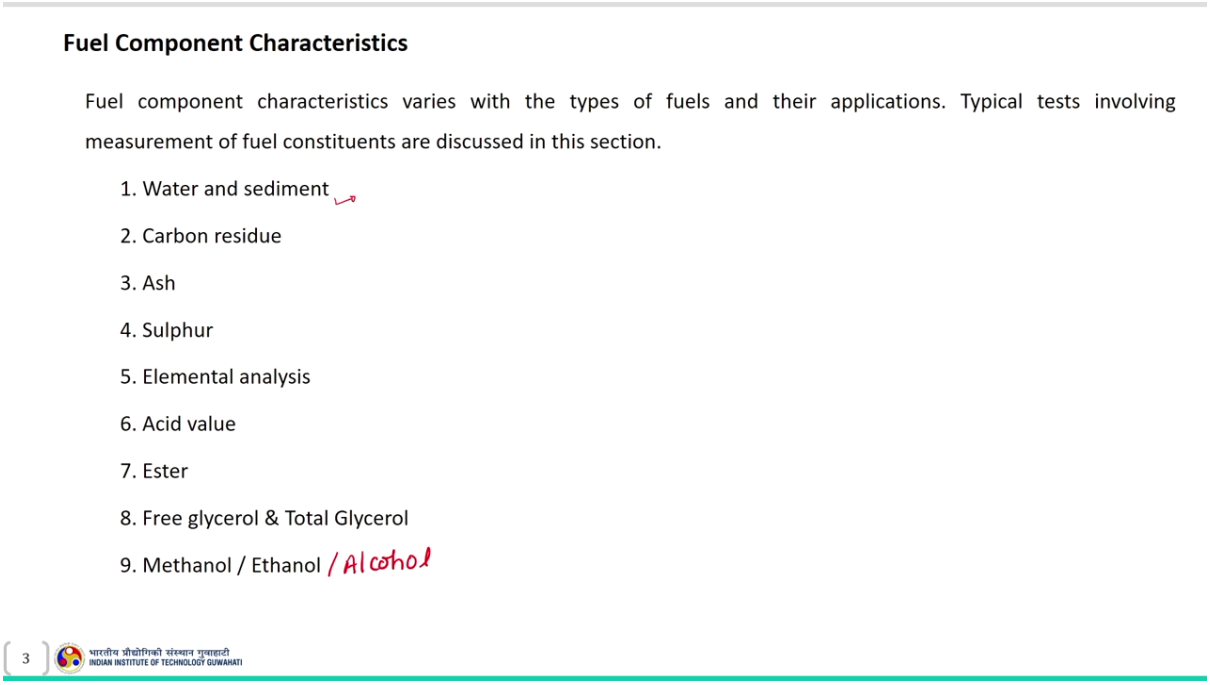
Lecture 11

Liquid fuels (Part II)

Good morning everyone.

Welcome to part two of the lecture two under module two. In this lecture we will discuss about the liquid fuels and their fuel component characteristics.

(Refer slide time: 00:38)

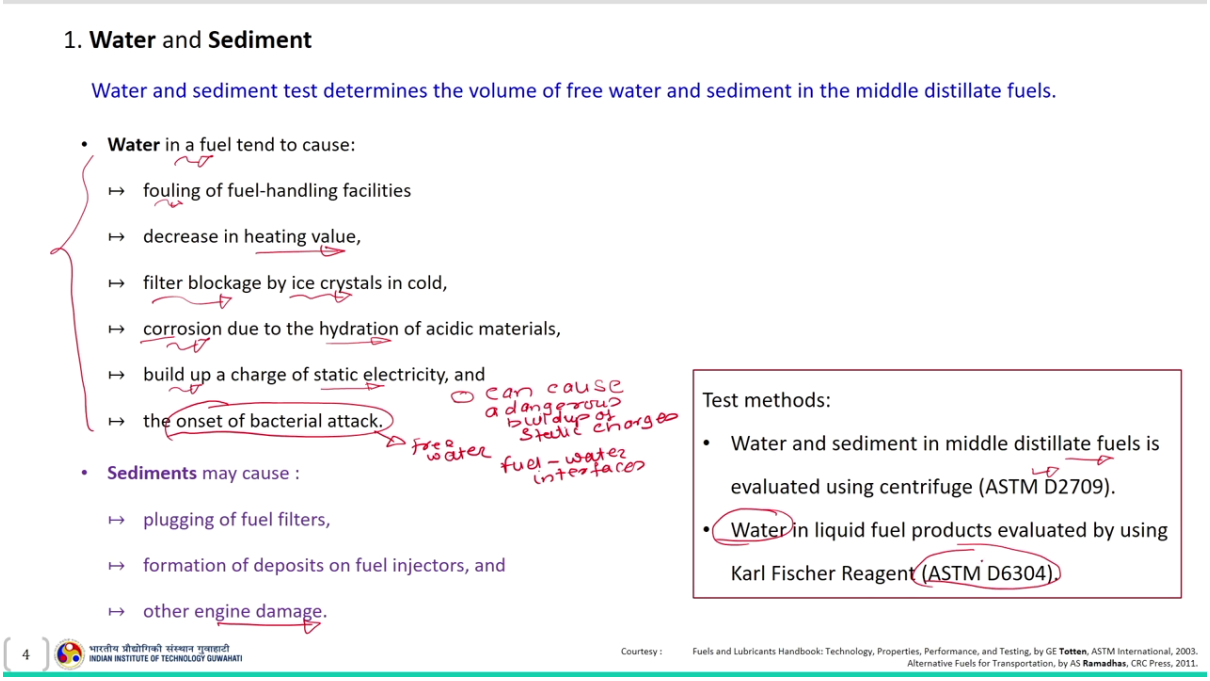


Fuel component characteristics vary with the types of fuel. For example, the fuel derived from coal and biomass as a source has varying different properties. Because these source materials itself have different component present in it.

So, the each component is used during this conversion process to convert into the liquid fuel or maybe the gaseous fuel. So, even there is a variation in the fuel as well. So, because of that there is a variation in the fuel component characteristics. So, the typical test which are

involved in the fuel component characteristics are discussed in this section and fuel component characteristic test include water and sediment, carbon residue, ash, sulphur content, elemental analysis, acid value of fuel or oil, ester content, free glycerol and total glycerol and last is methanol or also we can say the alcohol content. So now let us discuss about this component characteristics one by one.

(Refer slide time: 02:00)

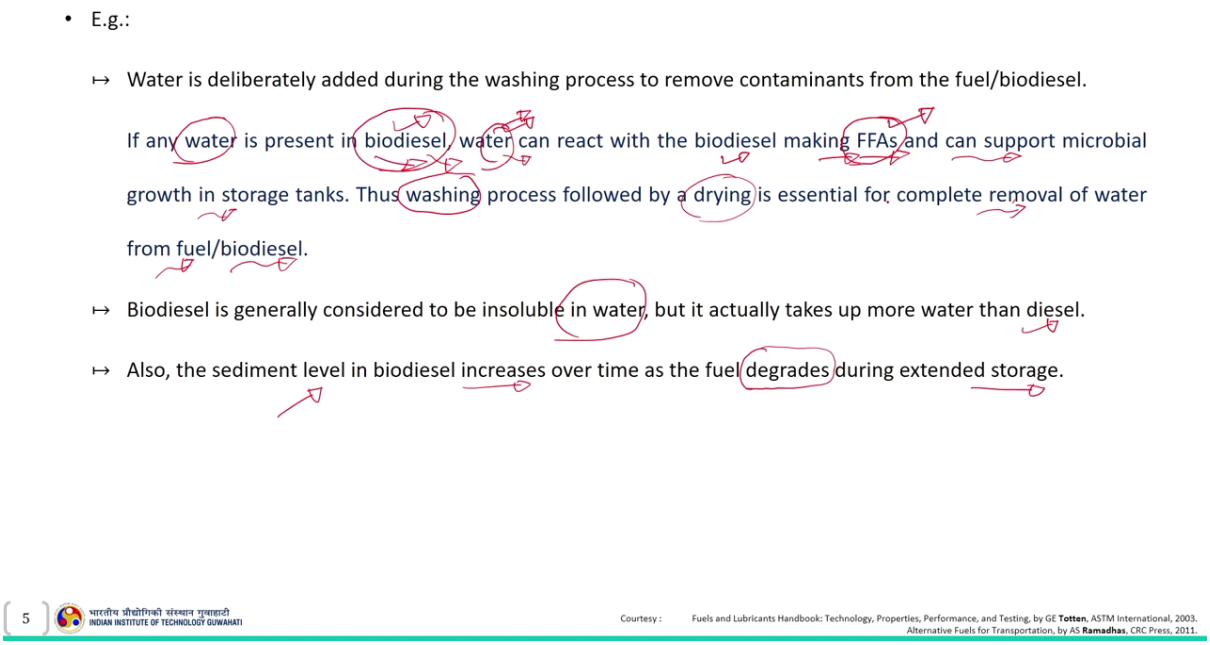


This method is used as an indication of free water and sediment suspended as hedge, cloudiness or droplets in the middle distillate fuels. Because the water in fuel it tends to cause falling of the fuel handling facilities and if the water is present in the fuel ultimately it decreases its heating value. Also, it may cause filter blockage by ice crystal. Because if the water is present in the fuel, so during cold condition it may form the ice crystals.

Also, it may cause corrosion due to the hydration of acidic materials or it may tend to build up a charge of static electricity. Because small amount of water here can cause a dangerous buildup of static charges. Apart from that the onset of bacterial attack, because the free water can support the microbial growth at fuel water interfaces in the fuel systems. Hence, the removal of water from the final fuel is essential to avoid this issue. Similarly, the sediment may cause plugging of the fuel filters, formation of deposits on the fuel injectors and also the other engine damages.

So, there are standard methods which are used to estimate this water and the sediment content in the fuel. So, the water and the sediment content in the metal distillate fuels is evaluated using this standard ASTM method. And only if the water contained in the fuel need to be estimated then it can be estimated using this standard method with the help of Karl Fischer's reagent. And this is one of the most popular techniques to know the water content in the fuel.

(Refer slide time: 04:46)



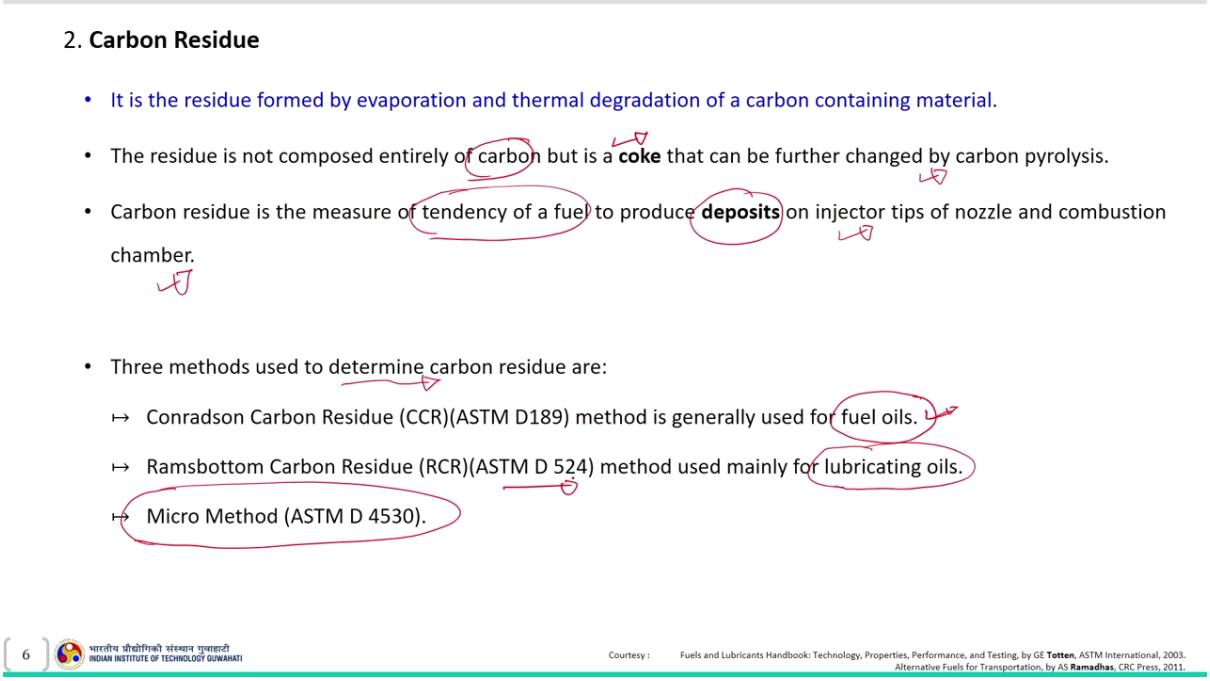
For example, sometimes water is deliberately added during the washing process to remove the contaminant and remaining impurities in the fuel or oil. Because, if any amount of water is present in say biodiesel, which is one of the popular liquid biofuel, then this water can react with the biodiesel and making FFA. Because, as we know the synthesis of biodiesel is a reversible reaction.

So, excess amount of water present in this reaction also can displace the equilibrium towards the formation of the free fatty acids. And the excess amount of water can also support the microbial growth in the storage tanks. So, as just mentioned before so the amount of water if it is in excess then it may also support the microbial growth in the storage tank.

Thus the washing process followed by drying is very essential for the complete removal of water from the fuel or I would say from the biodiesel as well. Because the biodiesel is generally considered to be insoluble in water, but it is actually takes up more water than even the conventional diesel.

Similarly, the sediment level in the biodiesel it increases over the time as the fuel degrades during the extended storage. And that is also one of the issues with the water having in the biodiesel. Because it may also increase the sediment level in the biodiesel during the extended storage period. Hence, it is essential to remove the water from the biodiesel before its use for the application purpose.

(Refer slide time: 06:46)



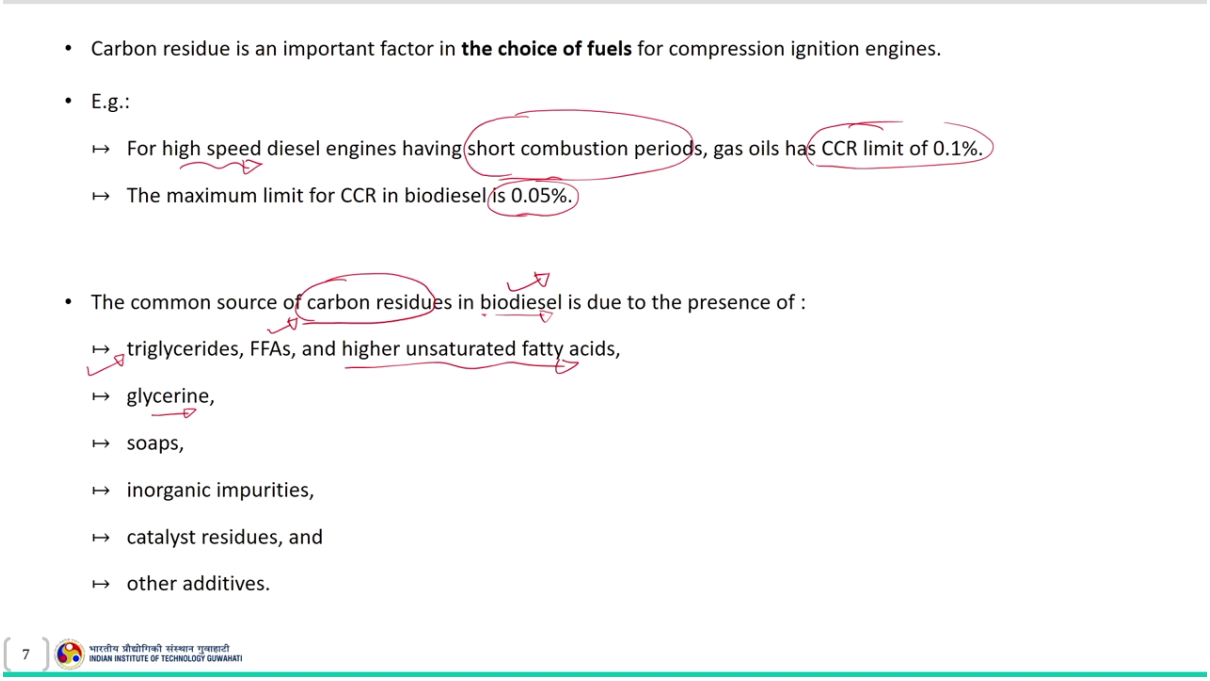
So, the next is the carbon residue. So, it is the residue which is formed by the evaporation and thermal degradation of the carbon containing material. And this residue is not composed entirely of carbon, but it is a coke. And that can be further changed by carbon pyrolysis. And this carbon residue is the measure of tendency of a fuel to produce deposits on injector tips of nozzle and the combustion chamber.

And there are methods available to estimate this carbon residue in the fuel. There are three methods which are used to determine the carbon residue, which includes the Conradsen

carbon residue method which is generally used for the fuel oils. And there is another method Ramsbottom carbon residue method which is used mainly for the lubricating oil. And there is another method which is called as a micro method. It is used to estimate the carbon residues in the fuel as well as the oil.

But if you are estimating the carbon residue content in the fuel oils, so it is prescribed to use this particular method. And when it is lubricating oil, then it is prescribed to use the second method for the estimation of the carbon residues in the given sample.

(Refer slide time: 8:15)

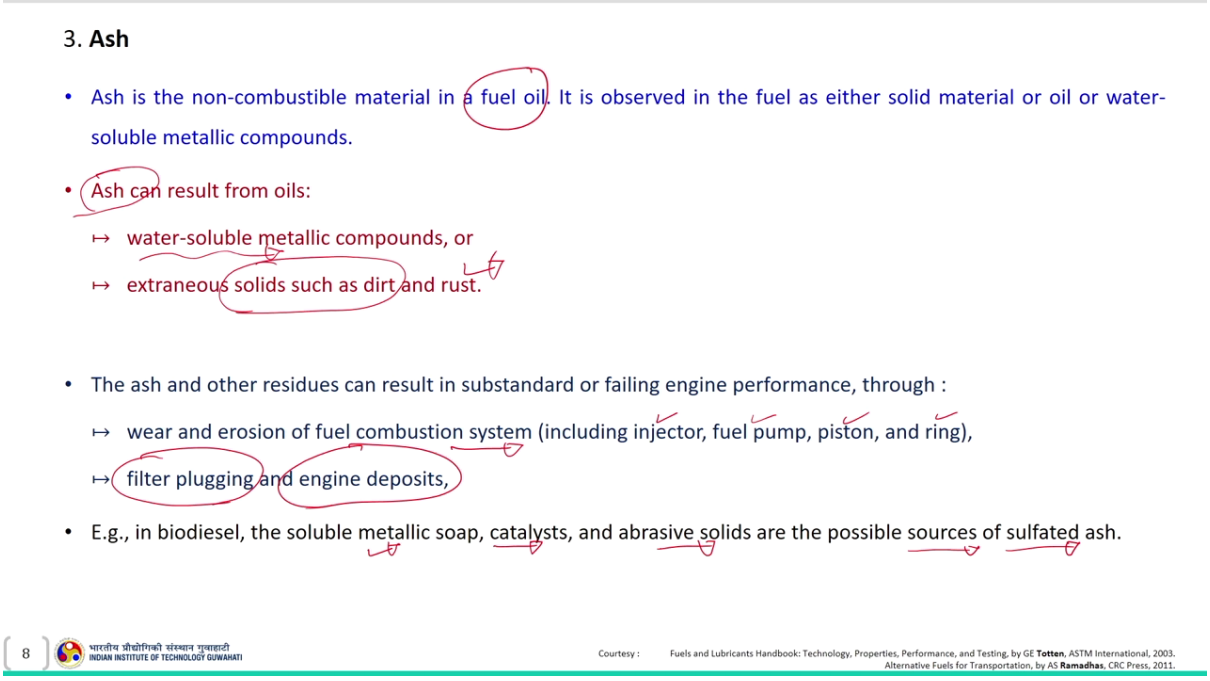


Carbon residue is also one of the important factors in selection of the fuel for compression ignition engine. Because for high speed diesel engines having a short combustion period the gas oil which has a CCR limit of 0.1% is preferred.

Similarly, the maximum limit of CCR in biodiesel is 0.05% only. And some common sources of carbon residue in the biodiesel is due to the presence of the triglyceride. If some amount of triglyceride is still left in the biodiesel then it is a cause of the formation of the carbon residues during its burning or combustion, even the FFAs and the higher unsaturated fatty acid.

If these are present in the biodiesel, then these are the major cause of formation of the carbon residues in the biodiesel as a fuel. Apart from the glycerin, soaps, inorganic impurities and the catalytic residues which are left in the biodiesel, it may a cause of formation of a carbon residue and other additives which are present in the source material.

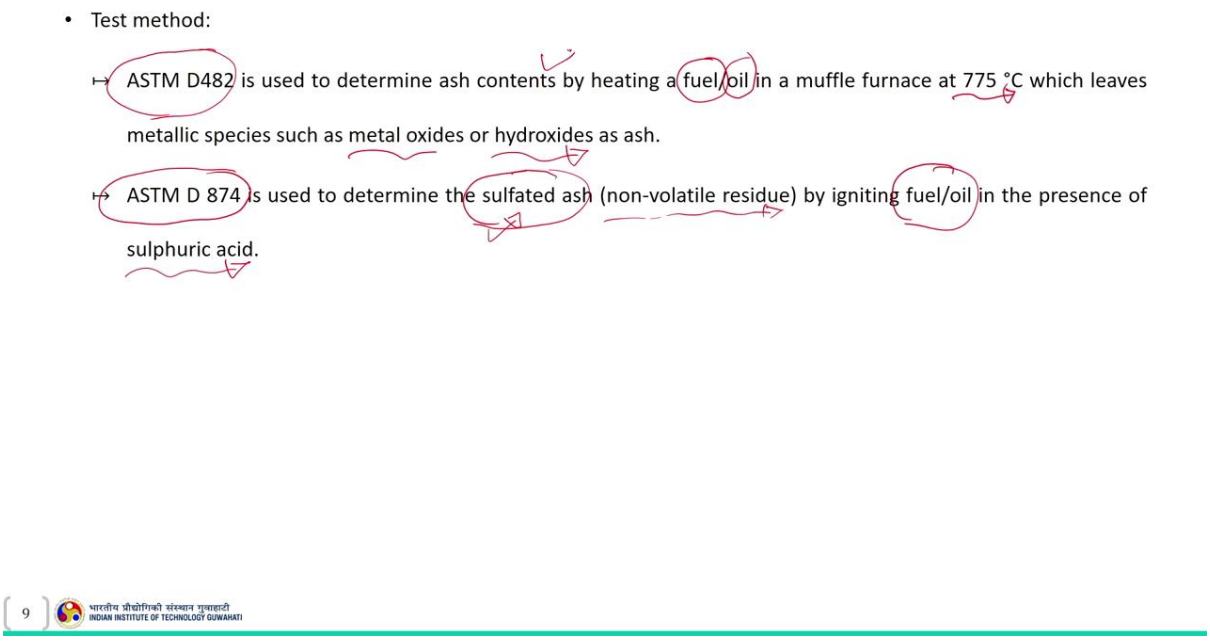
(Refer slide time: 9:31)



Ash is the non-combustible material in the fuel oil. It is observed in the fuel oil as solid material or oil or water soluble metallic compounds. And this ash, it can result from oils which are having the water soluble metallic compound as well as some external solid in the form of dirt and rust. So, if these are present in the oil then these are also cause of the ash content in the fuel oil.

The ash and other residues can also result in the substandard or failing engine performance. That means poor performance of the engine through wear and erosion of the fuel combustion system including the injector, fuel pump, piston and the ring, apart from that the filter plugging and the engine deposits. Example, in biodiesel the soluble metallic soap catalyst and the abrasive solids are the possible sources of sulfated ash which also contributes to the total ash content in the fuel oil.

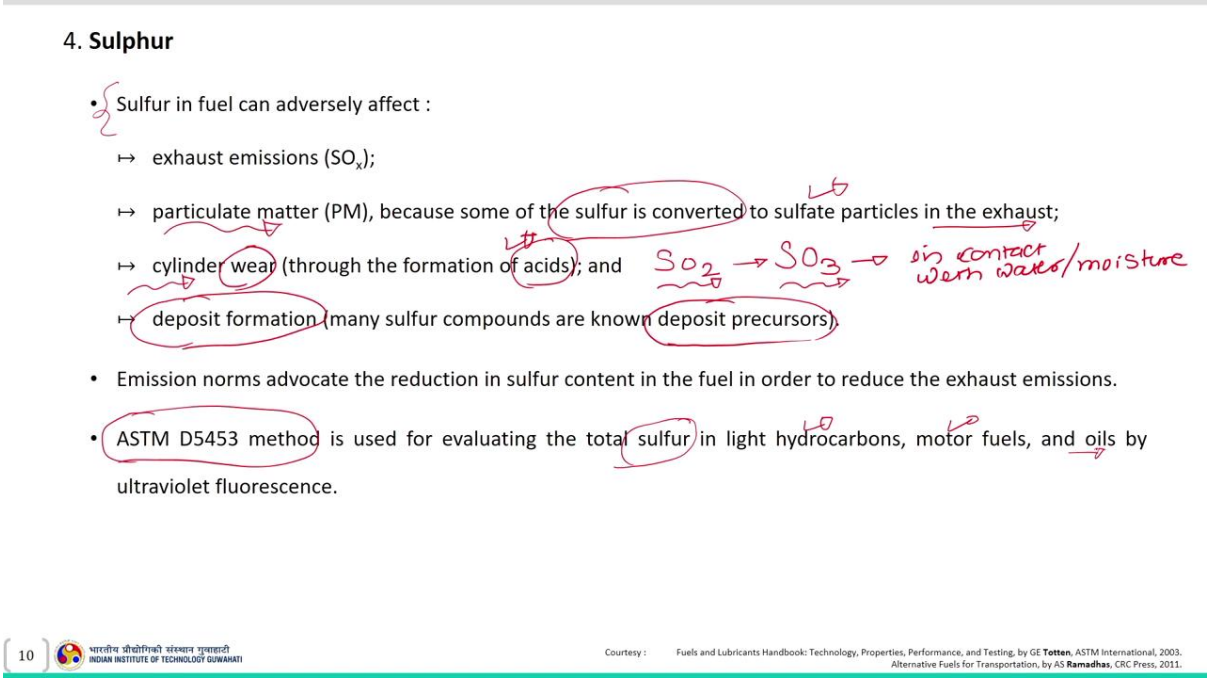
(Refer slide time: 10:56)



And these are the standard methods which are used to determine the ash content in the given sample. So, this ASTM method it is used to determine the ash content by heating the fuel or oil in a muffle furnace at around this particular temperature and which leaves the metallic species such as metal oxides and hydroxide as ash at the end of the process in the pan.

Similarly, this ASTM method it is also used to determine the sulphated ash, which is also known as non-volatile residue by igniting the fuel and the oil in presence of sulphuric acid. So, these are the two different methods which are used to determine the ash content in the given fuel sample. If we need to estimate the sulphated ash content then this method need to be used. And if you are just estimating the ash content in the form of these oxides of metal and the hydroxides then the first method is preferred.

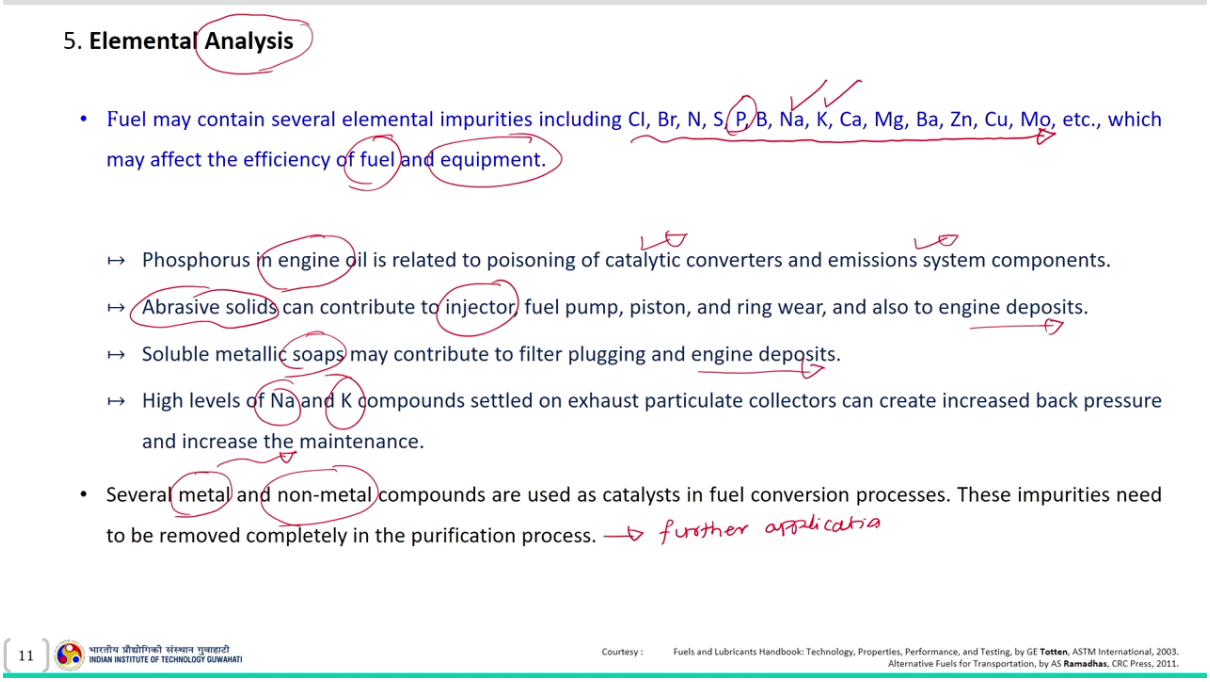
(Refer slide time: 12:10)



This sulphur content in the fuel it adversely affect the particulate matter because some of the sulphur is converted to sulphate particle in the exhaust. Similarly, it may cause the cylinder wear through the formation acid because this sulfur dioxide can further be oxidized to form sulfur trioxide which in turn forms sulfuric acid in contact with water or we can say moisture. And hence it may cause the cylinder wear because of the formation of this acid.

Deposit formation, because the many sulphur compounds are known deposit precursors. If fuel contains some amount of sulphur then it may cause deposit formation. Because of that the stringent norms are in place which advocates the reduction in the sulphur content in the fuel in order to reduce the exhaust emission. And this standard ASTM method it is used to evaluate the total sulphur content in the light hydrocarbon fuels, motor fuels and oils by ultraviolet fluorescence.

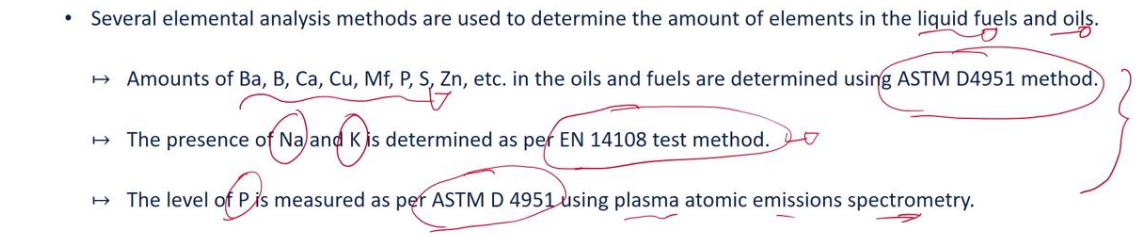
(Refer slide time: 14:00)



And another important characteristic is the elemental analysis because the fuel may contain several elemental impurities in the form of these following elements which may affect the efficiency of fuel and equipment. For example, say phosphorus. Phosphorus in engine oil relates to the poisoning of catalytic converter and emission system components.

Similarly, the abrasive solids can also contribute to injector, fuel pump, piston and ring wear and also to the engine deposits. Apart from that the soluble metallic soap may contribute to the filter plugging and the engine deposits. As well as high level of sodium and the potassium compounds settle on exhaust particulate collectors can create increased back pressure and also increase the maintenance. Several metal as well as the non-metal compounds are used as catalysts in the fuel conversion processes and these impurities need to be removed completely in the purification process before using this produce fuel for further application.

(Refer slide time: 15:52)

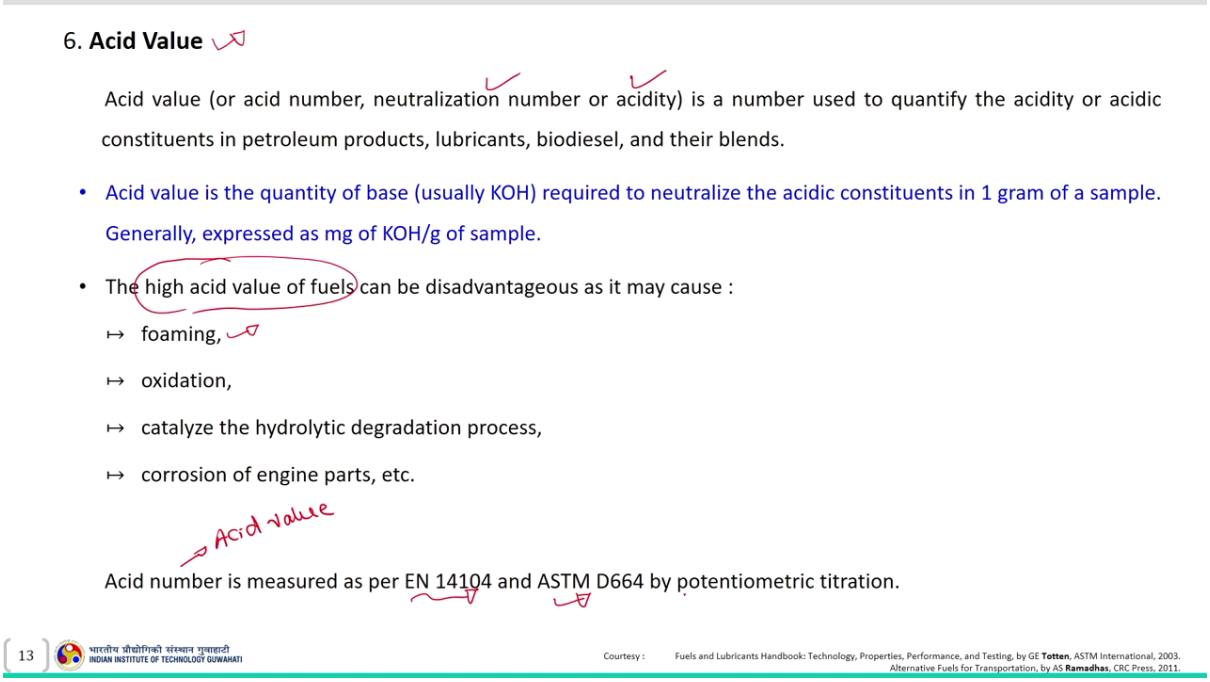


There are different elemental analyses methods are used to determine this amount of elements in the liquid fuels or oils. To estimate this following elements this standard ASTM method is used and for the estimation of sodium and the potassium this European standard test method is used.

And if you just need to estimate the phosphorus level in the liquid fuel and oil then it can be measured using this standard ASTM method using plasma atomic emission spectrometry. So, these are some standard techniques which are used to estimate the amount of this element in the liquid fuel or oil. But these are element specific method.

If you have to just estimate the sodium and the potassium, then it is advised to use this method. And if only phosphorus need to be estimated, then this following ASTM method can be used.

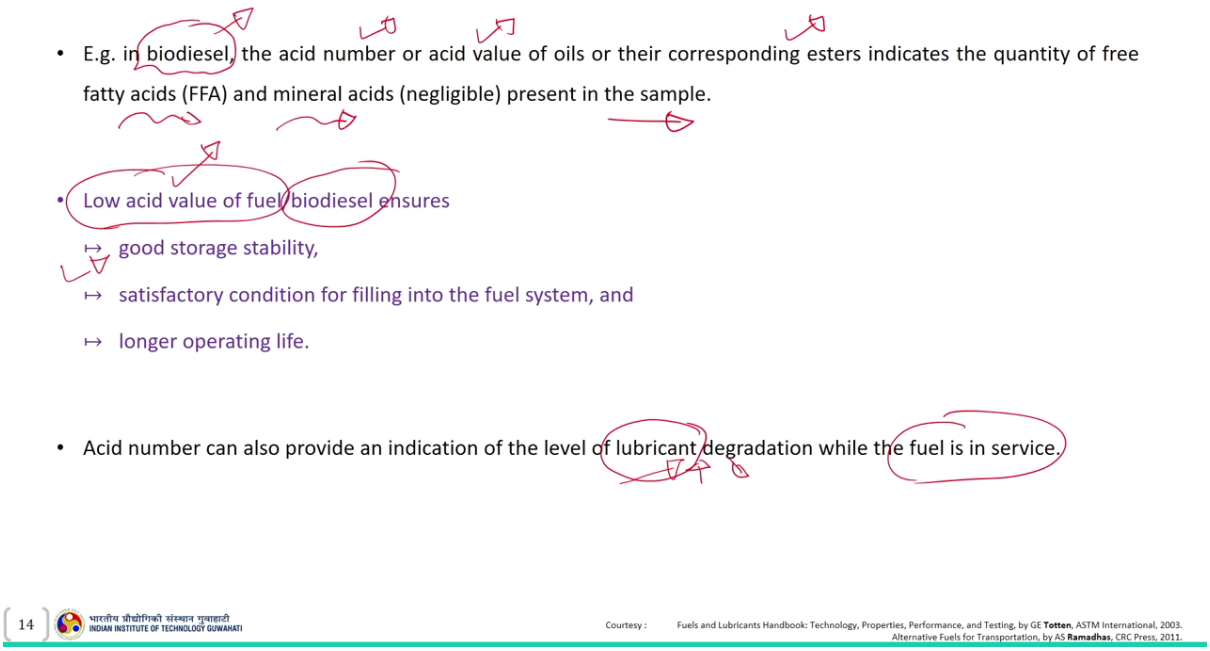
(Refer slide time: 17:05)



And the next is the acid value. The acid value is used to quantify the amount of base which is required to neutralize the acidic constituents in 1 gram of sample. And it is generally expressed as milligram of KOH per gram of sample. The high acid value of fuel can be disadvantages as it may cause the foaming oxidation.

And also catalyze the hydrolytic degradation processes and also the corrosion of engine parts. And this acid number which is also known as acid value or neutralization number or acidity is estimated as per these two standard methods by potentiometric titration.

(Refer slide time: 18:10)



For example, if we need to estimate the acid value of biodiesel, then it is the acid number or the acid value of oil or their corresponding esters indicating the quantity of free fatty acids and the mineral acids present in the sample. So, this particular technique is commonly used during the synthesis of biodiesel where we try to estimate the acid value of a sample to know whether the reaction has reached to a completion.

Low acid value of fuel or biodiesel ensures the good storage stability of a fuel, the satisfactory condition for filling into the fuel system and longer operating life. And it also provide an indication of the level of lubricant degradation while the fuel is in service because if the acid value of a given fuel is high then it may be a cause of lubricant degradation when the fuel is in service. Therefore, acid value needs to be maintained in the prescribed standard limit to avoid these further issues.

(Refer slide time: 19:41)

7. **Ester**

Biodiesel (known as FAME / fatty acid methyl ester) is composed of different ester compounds (monoalkyl esters of long-chain fatty acids).

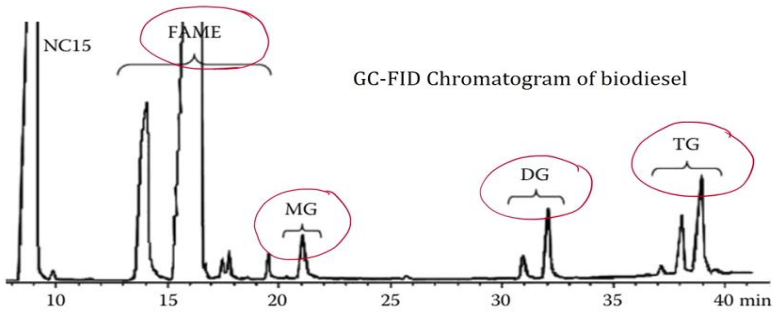
- The biodiesel contains methyl esters in the range of C6:0 to C24:1.
- Ester content characterize :
  - ↦ the purity of biodiesel,
  - ↦ degree of completion of transesterification, and
  - ↦ suitability of biodiesel for engine application.
- Typical biodiesel contains ~ 97% of esters and small amounts of mono, di, tri-glycerides.

Courtesy : Alternative Fuels for Transportation, by AS **Ramadhas**, CRC Press, 2011.

The measurement of ester content is essential in case of biodiesel. Because biodiesel is composed of different ester compounds and mostly monoalkyl esters of long chain fatty acids. And this biodiesel it contains the methyl esters in the range of C6 to C24 and this ester content it is also helpful to characterize the purity of biodiesel, also the degree of completion of transesterification, and suitability of biodiesel for the engine application. Because the typical biodiesel contains nearly 97% of esters and small amount of mono di and triglycerides.

(Refer slide time: 20:54)

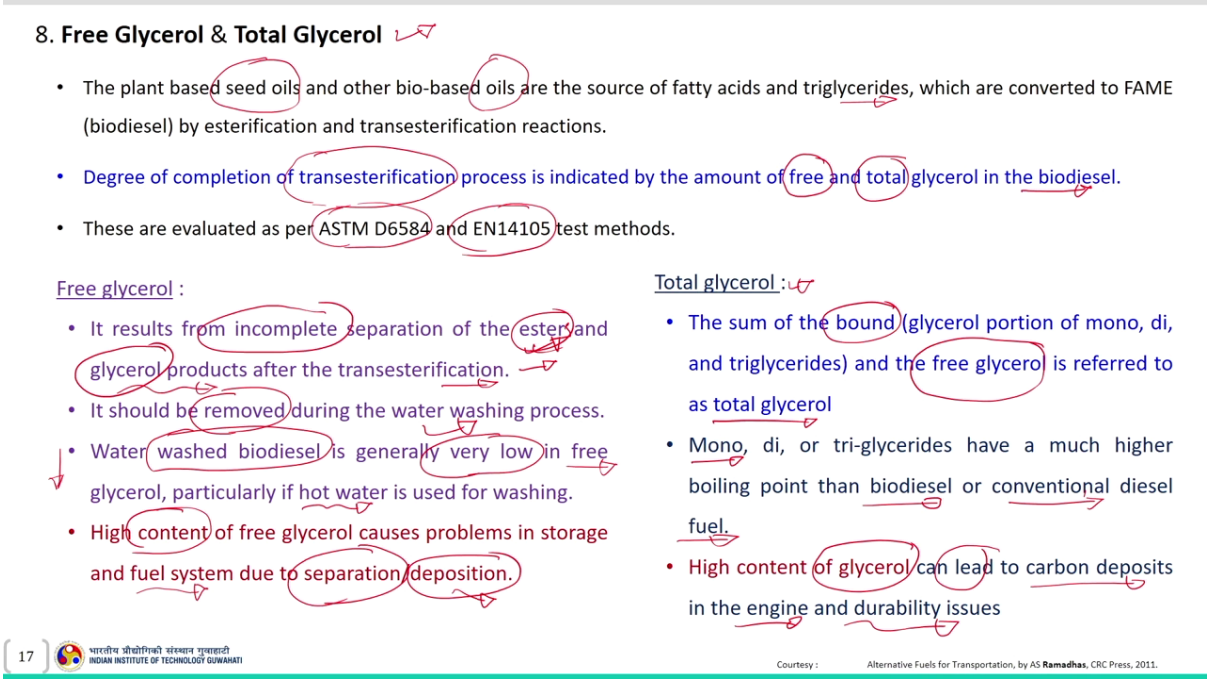
- The amount of esters in the biodiesel is determined as per **EN 14103** by gas chromatography.



Courtesy : Alternative Fuels for Transportation, by AS **Ramadhas**, CRC Press, 2011.

And the amount of this mono, di and triglycerides along with the esters can be estimated using the standard European method by gas chronography. And these peaks here represent the mono, di and triglyceride content in the biodiesel along with the fatty acid methyl ester content. And this is one of the most popular techniques to know the fatty acid methyl ester content in the biodiesel sample.

(Refer slide time: 21:23)



So, next is the glycerol. So, as we know this plant based seed oils and other bio based oils are the source of free fatty acids and triglycerides, which are converted to fatty acid methyl ester by esterification followed by transesterification reaction. And this degree of completion of transesterification reaction is indicated by the amount of free and total glycerol in the biodiesel.

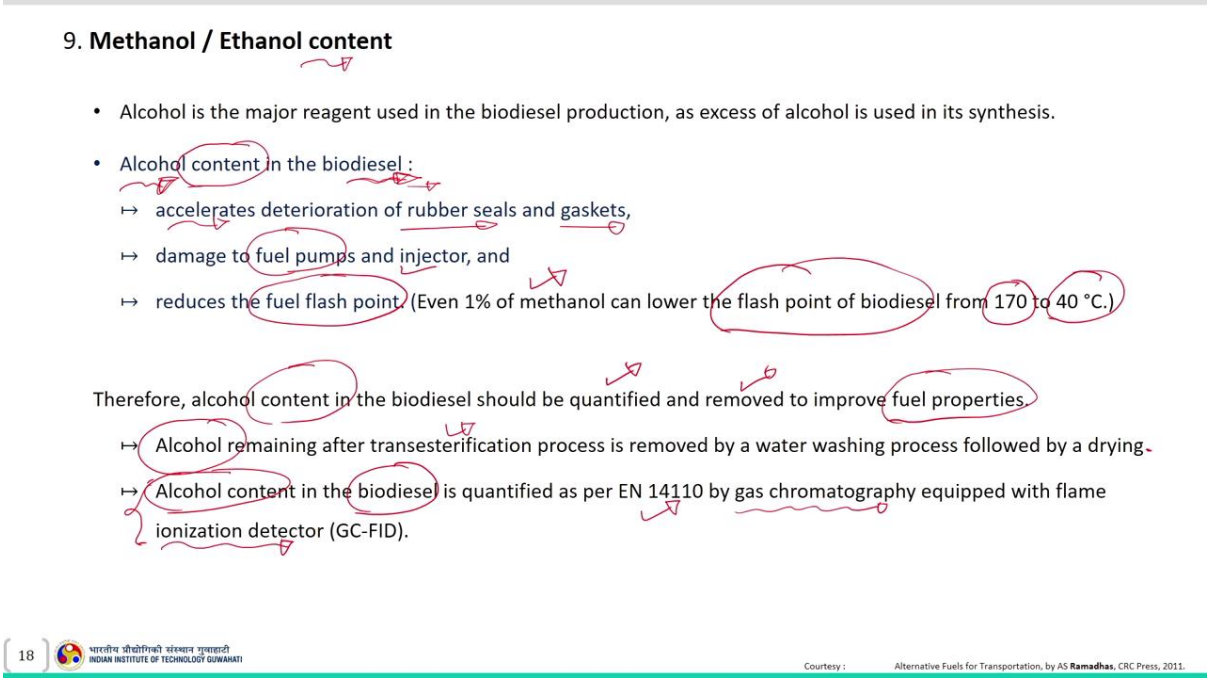
And this content of free and total glycerol are evaluated as per this standard ASTM and the European method. Here the free glycerol it mainly results from the incomplete separation of esters and glycerol products after the transesterification reaction. Because at the end of the transesterification reaction the mixture is allowed to settle and separate the glycerol fraction from the esters.

And the remaining glycerol in the ester should be removed during the water washing process. Water washed biodiesel is generally very low in the free glycerol content, particularly if hot water is used for the washing purpose. That means, if the hot water is used during the washing operation, then the washed biodiesel obtained at the end of this washing process is generally very low in the free glycerol content. Because during this washing process most of the glycerol gets removed from the ester phase. And the high content of free glycerol causes problems in the storage and the fuel system due to separation and the deposition.

So, as I mentioned because at the end of the transesterification process, the mixture is allowed to settle and separate the glycerol from the ester phase. And if some amount of the free glycerol still remains into the ester phase then it may cause problem in the storage and the fuel system. Because the glycerol has a tendency to separate from the ester phase and form a separate layer and as a result it may form a deposition in the storage tank as well as in the fuel system.

Similarly, the total glycerol it is the sum of bound and the free glycerol which is referred as a total glycerol. The mono, di and the triglycerides which have a much higher boiling point than biodiesel or even the conventional diesel fuel. Even the high content of glycerol it may lead to carbon deposits in the engine and also may have the durability issues. Therefore, the removal of the glycerol at the end of the transistor fusion process is essential to avoid these issues during operation of a biodiesel in the engine as well as in the fuel system.

(Refer slide time: 25:10)



And the next in the list is the alcohol content. Alcohol is a major reagent used in the biodiesel synthesis process as an excess of alcohol is used during the synthesis process. Because as we know this process is a reversible process.

Hence to displace the equilibrium towards the formation of the methyl ester excess amount of alcohol is used. Alcohol content in the biodiesel, asclerate, deterioration of the rubber seals and gaskets, also it may cause damage to the fuel pumps and the injector and also reduces the flash point. Because even 1% of the methanol in the biodiesel can lower the flash point of the biodiesel from 170 to 40 °C. Therefore, alcohol needs to be removed from the biodiesel before utilizing it into the engine system.

Similarly, the alcohol content in the biodiesel it should be quantified and removed to improve fuel properties as well. And this alcohol which is remaining after the transesterification process is removed by water washing process followed by drying. And this alcohol content in the biodiesel is quantified as per this European method which is mostly by the gas chromatography with flame ionization detector. So, this is also one of the convenient methods to estimate the alcohol content in the biodiesel. This covers most of the fuel component characteristic test which are majorly used for the liquid fuel.

Apart from that there are several other techniques and methods are used for the fuel component characteristics. But those are fuel specific and are not discussed in this section.

So, with this we will end this lecture here. So, in the next lecture we will practice few examples on the concept discussed in module 2.

Thank you.