

Energy Conversion Technologies (Biomass and Coal)

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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.

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Fuel Component Characteristics

Fuel component characteristics varies with the types of fuels and their applications. Typical tests involving measurement of fuel constituents are discussed in this section.

1. Water and sediment ✓
2. Carbon residue
3. Ash
4. Sulphur
5. Elemental analysis
6. Acid value
7. Ester
8. Free glycerol & Total Glycerol
9. Methanol / Ethanol / *Alcohol*

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.

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1. Water and Sediment

Water and sediment test determines the volume of free water and sediment in the middle distillate fuels.

- **Water** in a fuel tend to cause:

- ⇒ fouling of fuel-handling facilities
- ⇒ decrease in heating value,
- ⇒ filter blockage by ice crystals in cold,
- ⇒ corrosion due to the hydration of acidic materials,
- ⇒ build up a charge of static electricity, and
- ⇒ the onset of bacterial attack.

- **Sediments** may cause :

- ⇒ plugging of fuel filters,
- ⇒ formation of deposits on fuel injectors, and
- ⇒ other engine damage.

Test methods:

- Water and sediment in middle distillate fuels is evaluated using centrifuge (ASTM D2709).
- **Water** in liquid fuel products evaluated by using Karl Fischer Reagent (ASTM D6304)

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 fouling 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.

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- E.g.:

- ⇒ Water is deliberately added during the washing process to remove contaminants from the fuel/biodiesel.

If any water is present in biodiesel, water can react with the biodiesel making FFAs and can support microbial growth in storage tanks. Thus washing process followed by a drying is essential for complete removal of water from fuel/biodiesel.

- ⇒ Biodiesel is generally considered to be insoluble in water, but it actually takes up more water than diesel.

- ⇒ Also, the sediment level in biodiesel increases over time as the fuel degrades during extended storage.

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 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.

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2. Carbon Residue

- It is the residue formed by evaporation and thermal degradation of a carbon containing material.
- The residue is not composed entirely of carbon but is a **coke** that can be further changed by carbon pyrolysis.
- Carbon residue is the measure of tendency of a fuel to produce **deposits** on injector tips of nozzle and combustion chamber.
- Three methods used to determine carbon residue are:
 - Conradson Carbon Residue (CCR)(ASTM D189) method is generally used for fuel oils.
 - Ramsbottom Carbon Residue (RCR)(ASTM D 524) method used mainly for lubricating oils.
 - Micro Method (ASTM D 4530).

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.

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- Carbon residue is an important factor in **the choice of fuels** for compression ignition engines.
- E.g.:
 - ⇒ For high speed diesel engines having short combustion periods, gas oils has CCR limit of 0.1%.
 - ⇒ The maximum limit for CCR in biodiesel is 0.05%.
- The common source of carbon residues in biodiesel is due to the presence of :
 - ⇒ triglycerides, FFAs, and higher unsaturated fatty acids,
 - ⇒ glycerine,
 - ⇒ soaps,
 - ⇒ inorganic impurities,
 - ⇒ catalyst residues, and
 - ⇒ other additives.

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.

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3. Ash

- Ash is the non-combustible material in a fuel oil. It is observed in the fuel as either solid material or oil or water-soluble metallic compounds.
- Ash can result from oils:
 - ⇒ water-soluble metallic compounds, or
 - ⇒ extraneous solids such as dirt and rust.
- The ash and other residues can result in substandard or failing engine performance, through :
 - ⇒ wear and erosion of fuel combustion system (including injector, fuel pump, piston, and ring),
 - ⇒ filter plugging and engine deposits,
- E.g., in biodiesel, the soluble metallic soap, catalysts, and abrasive solids are the possible sources of sulfated ash.

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.

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- Test method:

→ ASTM D482 is used to determine ash contents by heating a fuel/oil in a muffle furnace at 775 °C which leaves metallic species such as metal oxides or hydroxides as ash.

→ ASTM D 874 is used to determine the sulfated ash (non-volatile residue) by igniting fuel/oil in the presence of sulphuric acid.

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.

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4. Sulphur

- Sulfur in fuel can adversely affect :
 - exhaust emissions (SO_x);
 - particulate matter (PM), because some of the sulfur is converted to sulfate particles in the exhaust;
 - cylinder wear (through the formation of acids); and $\text{SO}_2 \rightarrow \text{SO}_3 \rightarrow$ in contact with water/moisture
 - deposit formation (many sulfur compounds are known deposit precursors).
- Emission norms advocate the reduction in sulfur content in the fuel in order to reduce the exhaust emissions.
- ASTM D5453 method is used for evaluating the total sulfur in light hydrocarbons, motor fuels, and oils by ultraviolet fluorescence.

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.

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5. Elemental Analysis

- Fuel may contain several elemental impurities including Cl, Br, N, S, P, B, Na, K, Ca, Mg, Ba, Zn, Cu, Mo, etc., which may affect the efficiency of fuel and equipment.
- Phosphorus in engine oil is related to poisoning of catalytic converters and emissions system components.
- Abrasive solids can contribute to injector, fuel pump, piston, and ring wear, and also to engine deposits.
- Soluble metallic soaps may contribute to filter plugging and engine deposits.
- High levels of Na and K compounds settled on exhaust particulate collectors can create increased back pressure and increase the maintenance.
- Several metal and non-metal compounds are used as catalysts in fuel conversion processes. These impurities need to be removed completely in the purification process. → further application

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.

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- Several elemental analysis methods are used to determine the amount of elements in the liquid fuels and oils.

⇒ Amounts of Ba, B, Ca, Cu, Mn, P, S, Zn, etc. in the oils and fuels are determined using ASTM D4951 method.

⇒ The presence of Na and K is determined as per EN 14108 test method.

⇒ The level of P is measured as per ASTM D 4951 using plasma atomic emissions spectrometry.

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.

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6. Acid Value ✓

Acid value (or acid number, neutralization number or acidity) is a number used to quantify the acidity or acidic constituents in petroleum products, lubricants, biodiesel, and their blends.

- Acid value is the quantity of base (usually KOH) required to neutralize the acidic constituents in 1 gram of a sample. Generally, expressed as mg of KOH/g of sample.

- The high acid value of fuels can be disadvantageous as it may cause :

- foaming,
- oxidation,
- catalyze the hydrolytic degradation process,
- corrosion of engine parts, etc.

Acid value
Acid number is measured as per EN 14104 and ASTM D664 by potentiometric titration.

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.

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- E.g. in biodiesel, the acid number or acid value of oils or their corresponding esters indicates the quantity of free fatty acids (FFA) and mineral acids (negligible) present in the sample.
- Low acid value of fuel/biodiesel ensures
 - ↳ good storage stability,
 - ↳ satisfactory condition for filling into the fuel system, and
 - ↳ longer operating life.
- Acid number can also provide an indication of the level of lubricant degradation while the fuel is in service.

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.

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7. Ester

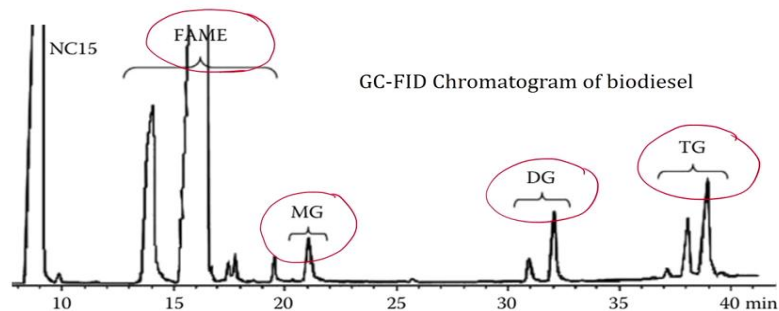
Biodiesel (known as FAME / fatty acid methyl ester) is composed of different ester compounds (monoalkyl esters of long-chain fatty acids).

- 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.

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.

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



And the amount of this mono, di and triglycerides along with the esters can be estimated using the standard European method by gas chromatography. 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.

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8. Free Glycerol & Total Glycerol

- The plant based seed oils and other bio-based oils are the source of fatty acids and triglycerides, which are converted to FAME (biodiesel) by esterification and transesterification reactions.
- Degree of completion of transesterification process is indicated by the amount of free and total glycerol in the biodiesel.
- These are evaluated as per ASTM D6584 and EN14105 test methods.

Free glycerol :

- It results from incomplete separation of the ester and glycerol products after the transesterification.
- It should be removed during the water washing process.
- Water washed biodiesel is generally very low in free glycerol, particularly if hot water is used for washing.
- High content of free glycerol causes problems in storage and fuel system due to separation/deposition.

Total glycerol :

- The sum of the bound (glycerol portion of mono, di, and triglycerides) and the free glycerol is referred to as total glycerol.
- Mono, di, or tri-glycerides have a much higher boiling point than biodiesel or conventional diesel fuel.
- High content of glycerol can lead to carbon deposits in the engine and durability issues.

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.

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9. Methanol / Ethanol content

- Alcohol is the major reagent used in the biodiesel production, as excess of alcohol is used in its synthesis.
- Alcohol content in the biodiesel :
 - accelerates deterioration of rubber seals and gaskets,
 - damage to fuel pumps and injector, and
 - reduces the fuel flash point. (Even 1% of methanol can lower the flash point of biodiesel from 170 to 40 °C.)

Therefore, alcohol content in the biodiesel should be quantified and removed to improve fuel properties.

- Alcohol remaining after transesterification process is removed by a water washing process followed by a drying.
- Alcohol content in the biodiesel is quantified as per EN 14110 by gas chromatography equipped with flame ionization detector (GC-FID).

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, accelerate, 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.