

Lecture-16

Biofuels and characteristics

Biofuels and Ethanol

“Biofuels” are transportation fuels like ethanol and biodiesel that are made from biomass materials. These fuels are usually blended with petroleum fuels namely with gasoline and diesel fuel, but they can also be used on their own. Ethanol and biodiesel are also cleaner burning fuels, producing fewer air pollutants. It has drawn significant attention due to increasing environmental concern and diminishing petroleum reserves. Bio-diesel fuel can be made from renewable vegetable oils, animal fats or recycled cooking oils by trans esterification process. Biodiesel is the fastest growing alternative fuel in the world. Ethanol is a alcohol fuel made from the sugars found in grains such as corn, sorghum, and wheat, as well as potato skins, rice, sugarcane, sugar beets and yard clippings by fermentation. 14.0 Characteristics of bio-fuels. The following are some of the characters for the efficient bio-diesel:

- a) Kinematic viscosity
- b) Density
- c) Calorific value
- d) Melt or pour point
- e) Cloud point
- f) Flash point
- g) Acid value
- h) Iodine value
- i) Cetane number
- j) Stability – oxidative, storage and thermal
- k) Carbon residue
- l) Ash percentage
- m) Sulphur percentage

Kinematic viscosity: Viscosity represents flow characteristics and the tendency of fluids to deform with stress. Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions.

Density: It's the weight per unit volume. Oils that are denser contain more energy. For example, petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per litre. Biodiesel is generally denser than diesel fuel with sample values ranging

between 877 kg/m³ to 884 kg/m³ compared with diesel at 835 kg/m³. Thus, density of the final product depends mostly on the feedstock used.

Calorific Value: Heat of combustion Heating Value or Heat of Combustion, is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is moisture content. Liquid biofuels however have bulk densities comparable to those for fossil fuels.

Melt point or Pour point Melt or pour point: It refers to the temperature at which the oil in solid form starts to melt or pour. In case where the temperatures fall below the melt point, the entire fuel system including all fuel lines and fuel tank will need to be heated.

Cloud point: The temperature at which an oil starts to solidify is known as the cloud point. While operating an engine at temperatures below an oil's cloud point, heating will be necessary in order to avoid waxing of the fuel.

Flash point (FP) : The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures are required for proper safety and handling of diesel fuel. The flash point determines the flammability of the material. Neat biodiesel has a flash point (150°C) well above the flash point of petroleum based diesel fuel ($\pm 70^\circ\text{C}$).

Acid value: The total acid number is an indication of the presence of free fatty acids formed due to oil degradation and combustion. It can also result from improper manufacturing, through remaining catalyst or excessive neutralization.

Iodine value: It is an index of the number of double bonds in biodiesel, and therefore is a parameter that quantifies the degree of unsaturation of biodiesel. It is reported in terms of the grams of iodine that will react with 100 grams of a fat or oil under specified condition. It is a value of the amount of iodine, measured in grams, absorbed by 100 grams of given oil. It is commonly used as a measure of the chemical stability properties of different biodiesel fuels against such oxidation.

Aniline point/Cetane number (CN): It is a relative measure of the interval between the beginning of injection and auto-ignition of the fuel. The higher the cetane number, the shorter the delay interval and the greater its combustibility. Fuels with low Cetane Numbers will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate better on fuels with Cetane Numbers above 50. Cetane number is usually measured directly using a test engine. Cetane tests provide information on the ignition quality of a diesel fuel. No.2 diesel fuel usually has a cetane rating between 45 and 50 while vegetable oil is 35 to 45. Biodiesel is usually have in between 50 to 60.

Stability: Biodiesel ages more quickly than petroleum diesel fuel due to the chemical structure of fatty acids and methyl esters present in biodiesel. Typically there are fourteen types of fatty acid methyl ester in the biodiesel. The individual proportion of presence of these esters in the fuel affects the final properties of biodiesel. Poor oxidation stability can cause fuel thickening, formation of gums and sediments which in turn can cause filter clogging and injector fouling. Thermal degradation occurs at high temperature and degrades hydroperoxide in the fuel more rapidly than oxidative degradation. Biodiesel and biodiesel blends are much more thermally stable than diesel. Biodiesel and its blends should not be stored in a storage tank or vehicle tank more than 6 months. Depending upon the storage temperature and other conditions suggest the use of appropriate antioxidants.

Carbon residue: This indicates the tendency of fuel to form carbon deposits in an engine. An important indicator of the quality of biodiesel is the carbon residue, which corresponds to the content of glycerides, free fatty acids, soaps, polymers and remaining catalyst.

Ash Percentage: Ash is a measure of the amount of metals contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. The ash content is important for the heating value, as heating value decreases with increasing ash content. Ash content for bio-fuels is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels.

Sulfur percentage : The percentage by weight, of sulfur in the fuel sulfur content is limited by law to very small percentages for diesel fuel used in on-road applications. First use vegetable oil and animal fat based biodiesel has less than 15 ppm sulphur. Many researchers claim that pure biodiesel is essentially sulphur free and therefore biodiesel is an ultra-low sulphur fuel.

Bio-diesel

Batch process

Preparation:

- 1) Care must be taken to monitor the amount of water and free fatty acids in the incoming bio-lipid (oil or fat). If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.
- 2) Catalyst is dissolved in the alcohol using a standard agitator or mixer.
- 3) The alcohol/catalyst mix is then charged into a closed reaction vessel and the biolipid (vegetable or animal oil or fat) is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol.
- 4) The reaction mix is kept just above the boiling point of the alcohol (around 70 °C) to speed up the reaction. Some systems recommend the reaction take place anywhere from room temperature

to 55 °C for safety reasons. Recommended reaction time varies from 1 to 8 hours; under normal conditions the reaction rate will double with every 10 °C increase in reaction temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters.

5) The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

6) Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

7) The by-product (i.e., glycerin) contains unused catalyst and soaps, that are neutralized with an acid and sent to storage as crude glycerin.

8) Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage.

Supercritical process

It is a catalyst-free method and continuous process. In this method, transesterification process uses supercritical methanol at high temperatures and pressures. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes.

Ultra- and high-shear in-line and batch reactors

Ultra- and High Shear in-line or batch reactors allow production of biodiesel continuously, semi-continuously, and in batch-mode. This method drastically reduces production time and increases production volume. The reaction takes place in the high-energetic shear zone of the ultra- and high Shear mixer by reducing the droplet size of the immiscible liquids such as oil or fats and methanol. Therefore, the smaller the droplet size, the larger the surface area the faster the catalyst can react.

Ultrasonic-reactor method

In the ultrasonic reactor method, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles constantly. This cavitation provides simultaneously the mixing and heating required to carry out the transesterification process. The ultrasonic reactor method for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day.

Microwave method

Current research is being directed into using commercial microwave ovens to provide the heat needed in the transesterification process. The microwaves provide intense localized heating that may be higher than the recorded temperature of the reaction vessel. A continuous flow process producing 6lt/min at a 99% conversion rate has been developed and shown to consume only one-fourth of the energy required in the batch process. Although it is still in the lab-scale, development stage, the microwave method holds great potential to be an efficient and cost-competitive method for commercial-scale biodiesel production.

Preparation of bio diesel from jatropha curcas

In most of the developed countries, biodiesel is produced from soybean, rapeseed, sunflower, peanut, etc., which are essentially edible in Indian context. Among the various vegetable oil sources, non-edible oils are suitable for biodiesel production. Because edible oils are already in demand and too expensive than diesel fuel. Among the non-edible oil sources, *Jatropha curcas* is identified as potential biodiesel source and comparing with other sources, which has added advantages as rapid growth, higher seed productivity, suitable for tropical and subtropical regions of the world. The *Jatropha* plant can reach a height up to 5 m and its seed yield ranges from 7.5 to 12 tonnes per hectare per year, after five years of growth. The oil content of whole *Jatropha* seed is 30-35 % by weight basis. Several properties of the plant including its hardness, rapid growth, easy propagation and wide ranging usefulness have resulted in its spread far beyond its original distribution. Preparation of bio diesel from *jatropha* requires a two-step approach; the extraction of the *Jatropha* oils from the seed, and the conversion of the extracted oil to Biodiesel, according to the following transesterification reaction. The mechanical extraction was done using a hydraulic press. After dehulling, the *Jatropha* seeds were first pressed to extract oil and then placed inside a soxhlet and brought into contact with a condensed solvent. The solvent dissolves the oil and then it is later separated using a rotor vapor. The obtained *Jatropha* oil was used for Biodiesel production. The transesterification reaction was done using methanol and two basic catalysts. Solvent extraction has higher oil yield than hydraulic press extraction.

Ethanol from agricultural produce (Sugar cane and corn)

Non-petroleum fuels liquid fuels find use when petroleum fuels are scarce or costly. The scientists have been in search of new fuels to replace conventional fuels that are used in IC engines. Among all the fuels, alcohols, which can be produced from sugarcane waste and many other agricultural products, are considered the most promising fuels for the future. There are two types of alcohols: methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$). Ethanol has attracted a lot of attention as a transport fuel because it is relatively cheap non-petroleum-based fuel. Also, the emissions from the combustion of ethanol are much less than for fossil fuels. Ethanol, being a pure compound, has a fixed set of physical as well as chemical properties. This is in contrast to

petrol and diesel, which are mixtures of hydrocarbons.. But in countries like India, ethanol is a strong candidate since they possess the agricultural resources for its production. It is a more attractive fuel for India because the productive capacity from sugarcane crops is high, of the order of 1345 l/ha. Earlier, this fuel was not used in automobiles due to low energy density, high production cost and corrosion. The current shortage of gasoline has made it necessary to substitute ethanol as fuel in SI engines. At present, Brazil is the only country that produces fuel alcohol on a large scale from agricultural products (mainly sugarcane). Brazil was the first and biggest producer of cheapest bio-ethanol in the world. Second cheapest bio-ethanol is made from corn in the USA. Properties of ethanol and methanol are similar, with difference of only 5 -10%. Ethanol is superior to methanol as it has wider ignition limit (3.5 -17) than methanol (2.15 -12.8). Ethanol calorific value (26,880 kJ/kg) is considerably higher than methanol (19,740 kJ/kg). Ethanol is a much more superior fuel for diesel engines as its cetane number is 8.

Compared to the cetane number of 3 for methanol, Ethanol is used in racing cars due to its very high heat of vaporization. 16.1 Manufacture of ethanol Three different feed stocks are available for ethanol production such as, sugar feed stock i.e., sugarcane and sugar beet; starch feed stock i.e., cereal grains and potato and cellulose feed stock i.e., forest products and agricultural residues. 16.1.1 Ethanol from starchy feed stock (grains) Ethanol production from cereal grains such as barley, wheat and corn is a much easier process than from cellulose material. The process includes several steps, as listed below:

- a) Milling of grains
- b) Hydrolysis of starch to sugar units
- c) Fermentation by yeast
- d) Distillation
- e) Removal of water from ethanol

After grinding the raw material, it is mixed with water and enzymes to break down the starch to sugar units. The free sugar can be used by yeast or bacteria and converted to ethanol and carbon dioxide. As the concentration of ethanol increases to about 15%, fermentation is reduced, since high alcohol concentration kills the yeast or bacteria. It is then necessary to separate the ethanol from the other material in the fermentation tanks by distillation. Distillation increases the ethanol concentration up to about 95%. In order to remove the rest of the water from the ethanol solution, it must be dried by different drying agents to a concentration of 99.5% ethanol or absolute ethanol. Extractive distillation with benzene also yields anhydrous ethanol. It is possible to produce 1 litre of absolute ethanol from about 3 kg of wheat.

Ethanol production from sugarcane is one of the easiest and most efficient processes since sugarcane contains about 15% sucrose. The glycosidic bond in the disaccharide can be broken down into two sugar units, which are free and readily available for fermentation. The cane is cut and the juice is extracted by maceration. After clarification, the juice is concentrated by boiling. The concentrated juice is fermented with yeast to produce raw ethanol. A series of distillation

steps including a final extractive distillation with benzene are used to obtain anhydrous ethanol. The normal yield of ethanol is about 8.73 litres of alcohol per tonne of cane. The potential of ethanol production in India is about 475 litres per year.