CHAPTER 3
PREPARATION AND PROPERTIES OF BIODIESEL

3.1 GENERAL

Bio-diesel is a domestic, renewable fuel for diesel engines derived from natural oils like vegetable oils. Bio-diesels can be used in any concentration with petroleum based diesel fuel in existing diesel engines with/without modifications. Bio-diesel is not the same thing as raw vegetable oil. It is produced by a chemical process, which removes glycerol from the oil.

Chemically, biodiesel is a fuel comprised of a mix of mono-alkyl esters of long chain fatty acids. A lipid transesterification production process is used to convert the base oil to the desired esters and remove free fatty acids. After this processing, unlike straight vegetable oil, bio-diesel has very similar combustion properties to petroleum diesel. However, it is most often used as an additive to petroleum diesel, improving the lubricity of pure ultra low sulphur petro-diesel fuel. It is one of the possible candidates to replace fossil fuels as the world’s primary transports energy source, because it is a renewable fuel that can replace petro-diesel in current engines and can be transported and sold using today’s infrastructure.

3.2 CHARACTERIZATION OF VEGETABLE OILS

The ideal diesel fuel molecule is of saturated non-branched hydrocarbon molecule with carbon ranging between 12 and 18. Vegetable oil molecules are triglycerides generally with non-branched chains of different lengths and different degree of saturation. It should also be noted that
vegetable oils contain substantial amount of oxygen in their molecular structure.

Fuel properties can be grouped conveniently into physical, chemical and thermal properties. Physical properties include viscosity, cloud point, pour point, flash point, boiling point and freezing point. Chemical properties comprise chemical structure, acid value, saponification value, sulphur corosions and thermal degradation. The thermal properties are distillation temperature, carbon residue and calorific value. The characteristics of vegetable oils fall within a fairly narrow band and are close to those of diesel. Vegetable oils have about 10% less heating value than diesel due to the presence of oxygen content in the molecules. However, the viscosity of oil is several times higher than that of diesel. The cetane number of most vegetable oils is in the range of 35-40.

The failure of neat oils as fuel is inherent in their structure and characteristics. Petroleum based diesel fuel has a different chemical structure from vegetable oils. Diesel fuel contains only carbon and hydrogen atoms, which can be arranged in straight chain, branched chain or aromatic configurations. Straight chain structures yield superior yield ignition quality. Vegetable oils have larger molecules, up to 4 times higher than that of diesel. The high viscosity of vegetable oils leads to poor atomization and incomplete combustion. At the time of combustion vegetable oil undergo oxidative and thermal polymerization and cause carbon deposition on the injector nozzles, ring sticking, lubricating oil dilution and degradation. The combination of high viscosity and low volatility of vegetable oil cause poor cold engine startup, misfire and ignition delay. So, it is understood that it is not only necessary to reduce the viscosity of oils but also minimize the undesirable properties of vegetable oil as fuel for diesel engines. These include reducing the chain length and reducing the unsaturation of vegetable oil molecules.
A natural organic compound found in the animal and vegetable fats are made up of various combinations of fatty acids (in sets of three) connected to a glycerol molecule, making them triglycerides. Each molecule of a fatty acid consists of a carboxyl group (oxygen, carbon and hydrogen) attached to a chain of carbon atoms with their associated hydrogen atoms. The number of carbon and hydrogen atoms in the chain determines the qualities of that particular fatty acid. The general formula of any oil is given by,

\[
CH_2 - OOC - R_1 \\
| \\
CH - OOC - R_2 \\
| \\
CH_2 - OOC - R_3
\]

The R- groups and -OOC- groups are contributed by the fatty acids, which contain 12-18 carbon atoms. Structurally, one molecule of glycerol reacts with three molecules of fatty acids to yield three molecules of water and a molecule of triglyceride. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds. When the three fatty acids are identical, the product is simple-triglyceride; when they are dissimilar, the product is a mixed-triglyceride. The vegetable oils are of mixed-triglycerides. Fully saturated triglycerides are solid at room temperature and thus are difficult to use as fuel, whereas the use of polyunsaturated triglycerides leads to excessive carbon deposits in engines. This is one of the most important considerations in adopting fuel formulation technique.

Diesel fuel contains both saturated and unsaturated hydrocarbons. The saturated hydrocarbons are present in large amounts as compared to unsaturated hydrocarbon in diesel. The higher saturation reduces the oxidation problem. Also, the aromatics are oxidation resistant. On the other hand, in the
case of vegetable oils, oxidation resistance is markedly affected by fatty acid composition. While, the large size of vegetable oil molecules and the presence of oxygen in the molecule lead to some fuel properties (such as viscosity) of vegetable oils to vastly differ from those of hydrocarbon fuels, due to similarities in molecular structures and C: H ratio, the use of vegetable oils in diesel engines seems to be justifiable suggestion.

In order to successfully utilize vegetable oils as CI engine fuels, either the engine has to be modified to operate on crude vegetable oil or the fuel has to be processed to become compatible with unmodified/existing engines. Engine modification can be effected by duel fueling, injection system modification and heated fuel lines. But, it requires more time and is expensive for vegetable oil specific systems owing to large number of engines already in use. Treatment of fuel is found to be more suitable and practicable. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosity, low volatility and polyunsaturated character. The problems have been reduced by developing vegetable oil derivatives that approximate the properties and performance and make them compatible with the hydrocarbon-based diesel fuels through: the heating of vegetable oils, blending, thermal cracking, micro-emulsion and transesterification.

3.3 DERIVATIVES OF TRIGLYCERIDES AS DIESEL FUELS

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon-based diesel fuels. The problems with substituting triglycerides for diesel fuel are mostly associated with their high viscosities, low volatilities and polyunsaturated character. These can be changed in at least four ways:

- Pyrolysis
3.3.1 Pyrolysis

Pyrolysis refers to a chemical change caused by the application of thermal energy in the presence of air or nitrogen spurge. Many investigators have studied the pyrolysis of triglycerides to obtained products suitable for diesel engines. These studies include the effect of temperature on the type of products obtained, the use of catalysts, largely metallic salts, to obtain paraffin and olefins similar to those present in hydrocarbon-based diesel fuels, the characterization of the thermal decomposition products.

Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatic and carboxylic acids.

Different types of vegetable oils produce large differences in the composition of the thermally decomposed oils. Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free radical or carbonium ion mechanism.

3.3.2 Micro Emulsification

Micro emulsifications are isotropic, clear, or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called co surfactant. The droplet diameters in micro emulsions range from 100 to 1000 Å. A micro emulsion can be made of vegetable oils with an ester and dispersant (co solvent), or of vegetable oils,
an alcohol and a surfactant, with or without diesel fuels. Micro emulsion because of their alcohol content have lower volumetric heating values than diesel fuels, but the alcohol have high latent heat of vaporization and tend to cool the combustion chamber, which would reduce nozzle coking. A micro emulsion of methanol with vegetable oils can perform nearly as well as bio-diesel fuels.

3.3.3 Dilution

Dilution of vegetable oils can be accomplished with such materials as diesel fuels, a solvent or ethanol. The dilution of sunflower oil with diesel fuels in the ratio of 1:3 by volume has been studied by engine tests were carried out by Ziejewski. The viscosity of this blend was 4.88 cSt at 40C. They conclude that the blend could not be recommended for long-term use in the direct injection diesel engines because of severe injector nozzle coking and sticking.

3.3.4 Transesterification

Transesterification of a vegetable oil was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Rudolf diesel’s prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany. This engine stood as an example of Diesel’s vision because it was powered by peanut oil a bio-fuel, though not strictly bio-diesel, since it was not Tran esterifies. He believed that the utilization of a biomass fuel was the real future of his engine.

During the 1920s, diesel engine manufacturers altered the engines to utilize the lower viscosity of the fossil fuel (petro-diesel) rather than vegetable oil, a biomass fuel. The petroleum industries were able to make inroads in fuel
markets because their fuel was much cheaper to produce than the biomass alternatives. The result was, for many years, a nearer elimination of the biomass fuel production infrastructure. Only recently have environmental impact concerns and a decreasing cost differential made biomass fuels such as bio-diesel a growing alternative.

In the 1900s, France launched the local production of biodiesel fuel (known locally as diester) obtained by the transesterification of rapeseed oil. It is mixed to proportion of 5% into regular diesel fuel, and to the proportion of 30% into the diesel fuel used by some captive fleets (public transportation). Renault, Peugeot and other manufacturers have certified truck engines for use with up to this partial bio-diesel. Experiments with 50% bio-diesel are underway.

From 1978 to 1996, the U.S. National Renewable Energy Laboratory experimented with using algae as a bio-fuel source in the “Aquatic Species Program”.

Transesterification, also called alcoholyis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than a alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides equation:

\[
\text{(Catalyst)} \\
\text{RCOOR'} + \text{R''OH} \quad \overset{\text{< >}}{\rightarrow} \quad \text{RCOOR''} + \text{R'OH} \\
\text{Ester} \quad \text{Alcohol} \quad \text{Ester} \quad \text{Alcohol}
\]

If methanol is used in the above reaction, it is termed methanolysis. The reaction of triglyceride with methanol is represented by the general equation:
3.4 SELECTED OILS FOR PRESENT WORK

Among the different vegetable oils, attention was focused on non-edible kind of oils for the present investigation. Karanja oil has been considered for the present work which is indigenous to India. Jatropha oil accepted world wide as best suited for biodiesel production. Indian government promotes the cultivation of these seeds by utilizing wastelands, which is available abundantly in all parts of our country. Even though sunflower oil, palm oil were consumed as edible oil in some regions of the country. When compared to these oils waste cooking oil has significant advantages both in availability and in price. The availability of cooked oils, which is wasted after utilization, is more, which is under utilized. It has huge potential in major cities of the countries, which can be used for biodiesel production. By taking all these factors in to account Jatropha oil, karanja oil,
sunflower oil, palm oil and waste cooking oil are chosen as a source for biodeiesel production.

3.5 STEPS FOR PREPARATION OF BIODIESEL

- Weight 6 kg of vegetable oil (refined sunflower oil) and pour it into the reactor for preliminary heating to temperature of about 60-70°C.

- In separate container, dissolve 22.8 grams of NaOH (3.8 grams per liter of oil, got by 3.5 grams stoichiometric equivalent and 0.3 grams for neutralizing FFA) in 1.2 L methanol (200 ml per liter of oil) add the NaOH slowly. This combined mixture makes sodium methoxide.

- Add this to the vegetable oil. Provide rigorous mixing with the use of a stirrer.

- The cloudy looking free fatty acids, called glycerine, will sink to the bottom and the methyl ester- a translucent liquid, will remain on top.

- Let the mixture settle overnight. Meanwhile another batch can be started as the reactor is not being used.

- The liquid on top is methyl ester, but before using it any remaining soaps or salts which could cause engine damage have to be removed.

- The glycerin which has sunk to the bottom can be used in production of cosmetics
3.6 PROPERTIES OF METHYL ESTERS

The properties of methyl esters produced were measured using respective standard techniques. It was found that the properties of all the methyl esters satisfy Indian standards (IS 15607:2005) for Biodiesels. The Properties of oil, methyl esters, diesel and Indian Standards for biodiesel are listed in Table 3.1 & 3.2.

Table 3.1 Properties of neat vegetable oils

<table>
<thead>
<tr>
<th>Property</th>
<th>Jatropha oil</th>
<th>Karanja oil</th>
<th>Sunflower oil</th>
<th>Palm oil</th>
<th>Waste cooking oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg/m³)</td>
<td>878</td>
<td>991</td>
<td>918</td>
<td>918</td>
<td>870</td>
</tr>
<tr>
<td>Kinematic viscosity c.stokes</td>
<td>49.9</td>
<td>69.6</td>
<td>58.5</td>
<td>39.6</td>
<td>5.03</td>
</tr>
<tr>
<td>Flash point (°c)</td>
<td>240</td>
<td>241</td>
<td>274</td>
<td>267</td>
<td>164</td>
</tr>
<tr>
<td>Fire point (°c)</td>
<td>266</td>
<td>253</td>
<td>299</td>
<td>296</td>
<td>160</td>
</tr>
<tr>
<td>Heating Value KJ/Kg</td>
<td>32430</td>
<td>34000</td>
<td>35620</td>
<td>36220</td>
<td>36940</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.878</td>
<td>0.912</td>
<td>0.9161</td>
<td>0.9180</td>
<td>0.9192</td>
</tr>
</tbody>
</table>
Table 3.2 Properties of oil after esterification

<table>
<thead>
<tr>
<th>Property</th>
<th>JTME</th>
<th>KME</th>
<th>SFOME</th>
<th>POME</th>
<th>WCOME</th>
<th>Diesel</th>
<th>IS for Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg/m²)</td>
<td>880</td>
<td>885</td>
<td>878</td>
<td>880</td>
<td>885</td>
<td>850</td>
<td>860-900</td>
</tr>
<tr>
<td>Kinematic viscosity c.stokes</td>
<td>5.27</td>
<td>5.72</td>
<td>10.3</td>
<td>6.2</td>
<td>5.7</td>
<td>3.5</td>
<td>2.5-6</td>
</tr>
<tr>
<td>Flash point(°c)</td>
<td>174</td>
<td>217</td>
<td>191</td>
<td>164</td>
<td>160</td>
<td>56</td>
<td>120</td>
</tr>
<tr>
<td>Fire point (°c)</td>
<td>190</td>
<td>223</td>
<td>197</td>
<td>171</td>
<td>164</td>
<td>63</td>
<td>130</td>
</tr>
<tr>
<td>Heating Value KJ/Kg</td>
<td>39174</td>
<td>36120</td>
<td>37250</td>
<td>38050</td>
<td>38650</td>
<td>42800</td>
<td>37270</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.8621</td>
<td>0.876</td>
<td>0.869</td>
<td>0.897</td>
<td>0.893</td>
<td>0.85</td>
<td>0.86-0.90</td>
</tr>
</tbody>
</table>

The photographs of neat oils and the corresponding methyl esters (biodiesels) are shown in Figures.

Fig. 3.2: Karanja oil and its methyl ester (KME)
Fig. 3.3: Jatropha oil and its methyl ester (JTME)

Fig. 3.4: Waste cooking oil and its methyl ester (WCO&ME)

Fig. 3.5: Palm oil and its methyl ester (PO&ME)
3.7 PRODUCTION COST OF METHYL ESTERS

The cost of vegetable oils and their methyl esters are given in the Table 3.3. The production cost of methyl ester derived from waste cooking oil is low because of less cost of waste cooking oil. The cost of methyl ester derived from Karanja oil is higher compared to that of methyl esters derived from Sunflower oil, Palm oil and jatropha oil due to the low yield of methyl ester from karanja oil.

**Table 3.3: Cost of methyl esters of selected oils**

<table>
<thead>
<tr>
<th>Type of oil</th>
<th>Cost of vegetable oil Rs./lit.</th>
<th>Cost of required methanol in Rs.</th>
<th>Cost of catalyst in Rs.3.75 grams</th>
<th>Yield of biodiesel in ml/lit of oil</th>
<th>Cost of biodiesel per litre in Rs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karanja</td>
<td>104</td>
<td>24</td>
<td>0.93</td>
<td>900</td>
<td>143.25</td>
</tr>
<tr>
<td>Jatropha</td>
<td>26</td>
<td>24</td>
<td>0.93</td>
<td>920</td>
<td>55.35</td>
</tr>
<tr>
<td>Sunflower</td>
<td>72</td>
<td>24</td>
<td>0.93</td>
<td>890</td>
<td>108.91</td>
</tr>
<tr>
<td>Palm</td>
<td>55</td>
<td>24</td>
<td>0.93</td>
<td>880</td>
<td>90.82</td>
</tr>
<tr>
<td>Waste cooking</td>
<td>20</td>
<td>24</td>
<td>0.93</td>
<td>910</td>
<td>49.37</td>
</tr>
</tbody>
</table>