CHAPTER-1
INTRODUCTION

1.1 ENERGY DEMAND

Today, more and more developing countries are prospering through economic reforms and are becoming industrially advanced. Energy is a basic requirement for the economic development of every country. Every sector of economy *viz.* agriculture, industry transport, commercial and domestic needs inputs of the energy. Diesel fuels play an important role in the industrial development of the country. These fuels run a major part of the transport sector and their consumption is steadily increasing. The intensity of fuel consumption is directly proportional to the development of the society. Diesel engines have been widely used as a power of engineering machinery, automobile and shipping equipment for their excellent drivability and thermal efficiency. Diesel fuels are used in heavy trucks, city transport buses, locomotive, electric generators, farm equipment, underground mine equipment etc.

The energy generated from the combustion of fossil fuels has indeed enabled many technological advancements and social-economic growth. However, it simultaneously creates many environmental concerns which can threaten the sustainability of our ecosystem. The use of fossil fuels is one of the major sources of world wide environmental pollution, the green house effect and acidification of both soil and the water. Also, the rising prices of oil and gas and its potential shortage in future may lead to the security of energy supply which is needed to sustain our economic growth. For example, India, like other developing countries of the world, despite its potential agricultural resources, is still highly dependent on imported crude oil for energy production. At present, India is importing more than 80% of its fuel demand, therefore, spending a huge amount of foreign currency on fuel. In India, the consumption of crude oil was about 184.68 metric ton (MT) for the year 2007-2008, but it has increased from
63% in 1971 (Table 1.1) [1-3]. With its growing population, India’s demand for the energy is about 3.5% of world’s energy demand and is expected to grow at the rate of 4.8% per annum. The demand of crude oil has increased dramatically, and thus, cost for the import of crude oil has increased substantially (Table 1.1).

Therefore, countries like India, not having these resources are facing a foreign exchange crisis, mainly due to import of crude oil. Thus, it is necessary to look for alternative fuels, which can be produced from materials available within the country. The high energy demand in the industrialized world and pollution problems caused due to widespread use of fossil fuels make it necessary to develop the renewable energy sources for limitless duration and smaller environmental impact than the traditional one.

Table 1.1. Production and consumption (MT) of crude oil in India [1-3]

<table>
<thead>
<tr>
<th>Year</th>
<th>Indigenous production</th>
<th>Import</th>
<th>Total</th>
<th>Import as % of total demand</th>
<th>Import value (in crores)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1971</td>
<td>6.8</td>
<td>11.7</td>
<td>18.5</td>
<td>63</td>
<td>107</td>
</tr>
<tr>
<td>1981</td>
<td>10.5</td>
<td>16.2</td>
<td>26.7</td>
<td>61</td>
<td>3349</td>
</tr>
<tr>
<td>1991</td>
<td>33.0</td>
<td>20.7</td>
<td>53.7</td>
<td>39</td>
<td>6118</td>
</tr>
<tr>
<td>2001</td>
<td>32.0</td>
<td>57.9</td>
<td>89.9</td>
<td>64</td>
<td>30695</td>
</tr>
<tr>
<td>2003-04</td>
<td>33.4</td>
<td>90.4</td>
<td>123.8</td>
<td>73</td>
<td>81000</td>
</tr>
<tr>
<td>2004-05</td>
<td>33.98</td>
<td>100.0</td>
<td>133.98</td>
<td>75</td>
<td>121500</td>
</tr>
<tr>
<td>2005-06</td>
<td>32.19</td>
<td>105.0</td>
<td>137.19</td>
<td>77</td>
<td>173076</td>
</tr>
<tr>
<td>2006-07</td>
<td>33.99</td>
<td>120.0</td>
<td>153.99</td>
<td>78</td>
<td>492000</td>
</tr>
<tr>
<td>2007-08</td>
<td>36.68</td>
<td>148.0</td>
<td>184.68</td>
<td>80</td>
<td>606800</td>
</tr>
</tbody>
</table>

1.2 VEGETABLE OIL AS FUEL

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Researchers have investigated for alternate fuel sources and concluded that vegetable oil based fuels can be used as alternative fuels [4]. Speaking to
the Engineering Society of St. Louis, Missouri, in 1912, Rudolph Diesel, said, “The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become in course of time as important as petroleum and the coal tar products of the present times” [5].

The vegetable oil can be used as fuels for diesel engines, but there are few problems with vegetable oil viz. its high viscosity than commercial diesel fuel [6]. The high viscosity of raw vegetable oil reduces fuel atomization and increases penetration, partially responsible for engine deposits, piston ring sticking, injector coking and thickening of oil [7,8]. Different methods have been developed to reduce the viscosity of vegetable oils such as dilution (blending), micro-emulsification, pyrolysis (thermal cracking), and transesterification.

### 1.2.1 Dilution (Blending)

Blending of vegetable oils with solvents decreases the viscosity, engine performance problems such as injector coking and more carbon deposits. The viscosity of oil can be lowered by blending with pure ethanol. Twenty-five parts of sunflower oil and 75 parts of diesel were blended as diesel fuel [9]. The viscosity was 4.88 cSt at 313K, while the maximum specified American standard test method (ASTM) value is 4.0 cSt at 313K. This mixture was not suitable for long term use in a direct injection engine. The viscosity decreases with increase in percentage of diesel.

### 1.2.2 Micro-emulsification

A micro emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1–150 range formed spontaneously from two normally immiscible liquids and one and more ionic or more ionic amphiphiles [10]. The engine performances were the same for a microemultion of 53% sunflower oil and the 25% blend of sunflower oil in diesel [11].
1.2.3 Pyrolysis (Thermal Cracking)

Pyrolysis is a method of conversion of one substance into another through heating or heating with the aid of the catalyst in the absence of air or oxygen [12]. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules [13]. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The liquid fuel produced from this process has almost identical chemical components to conventional diesel fuel [14].

1.2.4 Transesterification

Transesterification is a chemical reaction between triglyceride and alcohol in the presence of a catalyst. It involves a sequence of three consecutive reversible reactions where triglycerides (TG) are converted to diglycerides (DG) and then DG are converted to monoglycerides (MG) followed by the conversion of MG to glycerol. In each step an ester is produced and thus three ester molecules are produced from one molecule of TG [15]. The transesterification reaction requires a catalyst such as sodium hydroxide to split the oil molecules and an alcohol to combine with the separated esters. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. However methanol is preferred because of its low cost. Figure 1.1 shows the transesterification reaction of TG with alcohol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. It also gives glycerol as a byproduct which has a commercial value. Here $R_1$, $R_2$, $R_3$ are long-chain hydrocarbons, sometimes called fatty acid chains. Normally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. When the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally to glycerol, 1 mole of fatty ester is liberated at each step (Figure 1.2) [16]. Complete steps in biodiesel production are shown in Figure 1.3.
Triglyceride + ROH $\leftrightarrow$ Diglyceride + RCOOR$_1$
Diglyceride + ROH $\leftrightarrow$ Monoglyceride + RCOOR$_2$
Monoglyceride + ROH $\leftrightarrow$ Glycerol + RCOOR$_3$

Figure 1.2. Steps in transesterification

Out of the aforementioned methods, transesterification is the most viable process adopted known so far for the lowering of viscosity.
1.3 BIODIESEL

Biodiesel is the alkyl ester of fatty acids, made by the transesterification of oils or fats, from plants or animals, with short chain alcohols such as methanol and ethanol in the presence of catalyst and glycerin is consequently a by-product from biodiesel production (Figure 1.1). Pure biodiesel or 100% biodiesel is referred to as B100. A biodiesel blend is pure biodiesel blended with petrodiesel. Biodiesel blends are referred to as BXX. The XX indicates the amount of biodiesel in the blend (i.e., a B90 blend is 90% biodiesel and 10% petrodiesel).

Table 1.2 shows the comparison of modern available alternate fuels for transportation [18]. It is clear from the table that esters from vegetable oils (biodiesel) are the best substitutes for diesel because they do not demand any modification in the diesel engine. Biodiesel can be produced using different catalysts. Different catalysts with their advantages and disadvantages are shown in Table 1.3.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Current availability</th>
<th>Future availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>Excellent</td>
<td>Moderate-poor</td>
</tr>
<tr>
<td>Compressed natural gas</td>
<td>Excellent</td>
<td>Moderate</td>
</tr>
<tr>
<td>Hydrogen fuel cell</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>Moderate</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

1.4 INFLUENCE OF THE DIFFERENT PARAMETERS ON THE BIODIESEL PRODUCTION

The parameters affecting the biodiesel production are molar ratio, reaction temperature, pressure, water content, and free fatty acid content. The most important variables affecting the methyl ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature.
**Table 1.3. Different catalysts used in biodiesel production with their advantages and disadvantages [19-28]**

<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>Example</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkali</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homogeneous</td>
<td>NaOH, KOH</td>
<td>High catalytic activity, low cost, favorable kinetics</td>
<td>Low free fatty acids (FFA) requirement, anhydrous conditions, saponification, emulsion formation, more waste water from purification, disposable</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>CaO, CaTiO₃, CaZrO₃, CaMnO₃, Ca₂Fe₂O₅, Al₂O₃/KI, alumina/silica supported K₂CO₃</td>
<td>Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes</td>
<td>Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost</td>
</tr>
<tr>
<td><strong>Acid</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homogeneous</td>
<td>Concentrated sulphuric acid</td>
<td>Catalyze esterification and transesterification simultaneously, avoid soap formation</td>
<td>Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>ZnO/I₂, carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, Nafion-NR50</td>
<td>Catalyze esterification and transesterification simultaneously, recyclable, eco-friendly</td>
<td>Low acid site concentrations, low microporosity, diffusion limitations, high cost</td>
</tr>
<tr>
<td><strong>Enzymes</strong></td>
<td></td>
<td>Avoid soap formation, nonpolluting, Easier purification</td>
<td>Expensive, denaturation</td>
</tr>
</tbody>
</table>

Candida antarctica fraction B lipase, Rhizomucor miehei lipase
1.4.1 Effect of Molar Ratio

The yield of alkyl ester increases when the molar ratio of oil to alcohol increases [29]. Ramadhas et al. [30] and Sahoo et al. [31] have reported 6:1 molar ratio during acid esterification and 9:1 vegetable oil-alcohol molar during alkaline esterification to be the optimum amount for biodiesel production from high FFA rubber seed oil and polanga seed oil, respectively. Meher et al. [32] have taken 6:1 molar ratio during acid esterification and 12:1 molar ratio during alkaline esterification. Instead of taking molar ratio, Ghadge et al. [33] and Tiwary et al. [34] have used volume as a measure of ratio. Higher molar ratio result in greater ester production in a shorter time.

1.4.2 Effect of Temperature

In the alkali transesterification reaction, the temperature maintained by the researchers during different steps range between 318 and 338K. The boiling point of methanol is 337.9K. Temperature higher than this will burn the alcohol and will result in much lesser yield. It has been observed that temperature higher than 323K has a negative impact on the product yield for neat oil, but has a positive effect for waste oil with higher viscosities [35].

1.4.3 Effect of Water and Free Fatty Acid Contents on the Yield of Biodiesel

Water can cause soap formation and frothing. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and made the separation of glycerol difficult [33, 36]. Kusdiana and Saka [37] are of the opinion that water has a negative effect than presence of free fatty acids and hence the feedstock should be water free. It was investigated that even a small amount of water (0.1%) in the transesterification reaction will decrease the ester conversion from vegetable oil [38, 39]. Presence of water and FFA in raw material resulted in soap formation and a decrease in yield of the alkyl
ester, consume catalyst and reduce the effectiveness of catalyst and presence of water had a positive effect in the yield of methyl esters when methanol at room temperature was substituted by supercritical methanol [40].

1.4.4 Effect of Catalyst Content

Presence of catalyst like calcium oxide (CaO) can accelerate the methyl ester conversion from sunflower oil at 525K and 24 MPa even if a small amount of catalyst (0.3% of the oil) was added [41]. The transesterification step accelerates with the increase in CaO content from 0.3% to 3%. However, further enhancement of CaO content to 5% produced little increase in the yield of methyl ester.

1.5 BIODIESEL PROPERTIES AND SPECIFICATIONS

Biodiesel standards identify the parameters the pure biodiesel must meet before being used as a pure fuel or being blended with petroleum based diesel fuel. Table 1.4 shows the various physico-chemical properties of biodiesel as per ASTM D-6751, European standard EN-14214 standard and Indian standard IS-15607 [42-45]. Usually ASTM standards are followed all over the world. All of these properties and their significance will be studied in detail in the coming chapters.

The physical properties of biodiesel are similar to those of diesel fuels. Viscosity is one of the most important properties of biodiesels as it affects the operation of fuel injection equipment (FIE), particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets [46]. As discussed earlier, the conversion of TG into methyl or ethyl esters through the transesterification process reduces the molecular weight to one third that of the triglyceride and reduces the viscosity by a factor of about eight. As the oil temperature increases its viscosity decreases [41].
### Table 1.4. Physico-chemical properties of pure biodiesel according to ASTM D-6751, EN-14214 and IS-15607 standards [42-45]

<table>
<thead>
<tr>
<th>Property (units)</th>
<th>ASTM D-6751 test method</th>
<th>ASTM D-6751 limits</th>
<th>EN-14214 test method</th>
<th>EN-14214 limits</th>
<th>IS-15607 test method</th>
<th>IS-15607 limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation stability at 110°C (h)</td>
<td>EN14112</td>
<td>Min. 3h</td>
<td>EN ISO 14112</td>
<td>Min. 6h</td>
<td>EN 14112</td>
<td>Min.6h</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>D 2500</td>
<td>-</td>
<td>EN ISO 23015</td>
<td>-</td>
<td>IS 1448 P:10</td>
<td>-</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>D 97</td>
<td>-</td>
<td>EN ISO 3016</td>
<td>-</td>
<td>IS 1448 P:10</td>
<td>-</td>
</tr>
<tr>
<td>Cold filter plugging point (°C)</td>
<td>D 6371</td>
<td>-</td>
<td>EN 116</td>
<td>Variable</td>
<td>IS 1448 P:10</td>
<td>-</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>D 93 Min.130</td>
<td>EN ISO 3679 Min. 120</td>
<td>IS 1448 P:21 Min.120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity at 40 °C (cSt)</td>
<td>D 445</td>
<td>1.9-6.0</td>
<td>EN ISO 3104 3.5-5.0</td>
<td>IS 1448 P:25 2.5-6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphated ash (% mass)</td>
<td>D 874 Max. 0.02</td>
<td>EN ISO 3987 Max. 0.02</td>
<td>IS 1448 P:4 Max.0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur (%mass)</td>
<td>D 5453/D 4294 Max.0.0015 (S15) Max 0.05 (S 500)</td>
<td>EN ISO 20846/20884 Max. 0.0010</td>
<td>ASTM D 5453 Max.0.005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper corrosion</td>
<td>D 130 Max. 3</td>
<td>EN ISO 2160 Max. 1</td>
<td>IS 1448 P:15 Max. 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetane number</td>
<td>D 613 Min. 47</td>
<td>EN ISO 5165 Min. 51</td>
<td>IS 1448 P:9 Min. 51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water and sediment (vol.%</td>
<td>D 2709 Max. 0.05</td>
<td>-</td>
<td>-</td>
<td>D 2709 Max. 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conradson carbon residue (CCR) 100% (%mass)</td>
<td>D 4530 Max. 0.05</td>
<td>EN ISO 10370 Max. 0.3</td>
<td>D 4530 Max. 0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutralization value (mg, KOH/g)</td>
<td>D 664 Max. 0.50</td>
<td>EN ISO 14104 Max. 0.5</td>
<td>IS 1448 P:1/Sec.1 Max. 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free glycerin (%mass)</td>
<td>D 6584 Max. 0.02</td>
<td>EN ISO 14105/14106 Max. 0.02</td>
<td>D 6584 Max. 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total glycerin (%mass)</td>
<td>D 6584 Max. 0.24</td>
<td>EN ISO 14105 Max. 0.25</td>
<td>D 6584 Max. 0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus (%mass)</td>
<td>D 4951 Max. 0.001</td>
<td>EN 14107 Max.0.001</td>
<td>D 4951 Max.0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillation temperature</td>
<td>D 1160 90% at 360 °C</td>
<td>-</td>
<td>-</td>
<td>Not under spec. Min 90%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 1.6 MAJOR SOURCES FOR BIODIESEL PRODUCTION

The major sources of biodiesel in the form of edible oils, non-edible oils, animal fats and some other are listed in Table 1.5 [16, 28, 33, 44, 47-78].
Table 1.5. Sources of biodiesel production [16, 28, 33, 44, 47-78]

<table>
<thead>
<tr>
<th>Edible oils</th>
<th>Non-edible oils</th>
<th>Animal fats</th>
<th>Other sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>Jatropha curcas</td>
<td>Lard</td>
<td>Algae</td>
</tr>
<tr>
<td>Sunflower</td>
<td>Pongamia pinnata</td>
<td>Tallow</td>
<td>Bacteria</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>Mahua</td>
<td>Poultry Fat</td>
<td>Fungi</td>
</tr>
<tr>
<td>Canola</td>
<td>Linseed</td>
<td>Fish oil</td>
<td>Tarpenes</td>
</tr>
<tr>
<td>Copra</td>
<td>Neem</td>
<td></td>
<td>Latexes</td>
</tr>
<tr>
<td>Barley</td>
<td>Jojoba</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coconut</td>
<td>Brassica carinata</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton seed</td>
<td>Rubber plant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Groundnut</td>
<td>Sesame</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oat</td>
<td>Salmon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td>Moringa oleifera</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorghum</td>
<td>Sesamum indicum</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Terminalia catappa</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Guizotia abyssinica</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.7 PERFORMANCE OF DIESEL ENGINES USING BIODIESEL

Number of researchers investigated the performance characteristics of different diesel engines using biodiesel. Raheman and Phadatare [67] used the blend of the karanja methyl ester and diesel to evaluate the diesel engine performance and found increase in torque, brake power, brake thermal efficiency and reduction in brake-specific, fuel consumption. Usta [79] showed that tobacco seed oil methyl ester can be partially substituted for the diesel fuel at most operating conditions in terms of performance parameter and emissions without any engine modification and preheating of the blends.

Carraretto et al. [80] studied the operation of a biodiesel fueled boiler for some months and stated that the biodiesel seems to be a promising solution for boilers with
only minor adjustments and the performances are comparable with oil operation. Kadiyala et al. [81] reported the peak cylinder pressure and rate of pressure rise with the use of pungam methyl ester and diesel fuel varied with marginal difference. The heat release rate curves, diffused combustion in the case of pungam methyl ester at full load running of the engine are comparatively better than diesel fuel. Kumar et al. [82] reported that brake thermal efficiency was better in the dual fuel operation and with the methyl ester of jatropha oil as compared to the blend. It increased from 27.4% with neat jatropha oil to a maximum of 29% with the methyl ester and 28.7% in the dual fuel operation.

Yarbrough et al. [83] investigated the performance of a diesel engine with six variants of sunflower oil as fuel. They reported the prevention of the engine failure with degummed and dewaxed vegetable oil. They also concluded that raw sunflower oil cannot be a fuel but modified sunflower oil can be used as a fuel for diesel engines. Performance characteristics of mahua oil (Madhuca indica) oil ethyl ester in a four stroke natural aspirated direct injection diesel engine were carried out by Sukumar et al. [84]. Results showed that brake thermal efficiency was comparable with diesel.

1.8 Emissions Using Biodiesel

Biodiesel mainly emits carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), oxides of nitrogen (NO\textsubscript{x}), sulphur oxides and smoke. A brief review has made about these pollutants emitted from biodiesel.

Chang et al. [85] studied the effects of blends of methyl and isopropyl ester of soybean oil with diesels in a four cylinder turbocharged John Deer 4276T engine on emissions of CO, hydrocarbon (HC), particulate matter (PM), and NO\textsubscript{x}. Both methyl and isopropyl ester provided significant reductions in PM emission as compared with diesel fuels. Emission of CO, and HC were also reduced significantly, but NO\textsubscript{x} increased by about 12%. Scholl, Nwafor and Rice [86] reported that lower emission of the unburnt HC emission when operated with the rapeseed methyl ester. The rapeseed oil methyl ester and diesel blend in a single cylinder diesel engine has been tested by Desantes et al. [87]. They reported that when the inlet air temperature had increased from ambient, the carbon
monoxide, and smoke emissions decreased considerably. The use of methyl esters of
sunflower oil, cottonseed oil, soybean oil and corn oil as fuel in a single cylinder direct
injection diesel engine had also been tested by Altin et al. [88].

Kumar et al. [89] observed reduction in smoke, hydrocarbon and CO emissions
with the induction of hydrogen, however, the NOX emissions increased due to higher
combustion rates. Dorado et al. [90] tested the use of methyl ester of used olive oil as fuel
in a direct injection diesel engine and reported that CO, CO2, NOX and sulphur dioxide
emissions decreased by 59, 8.6, 32 and 57% respectively and that the smoke emission
was low. Raheman and Phadatare [67] tested karanja methyl ester and its blends with
diesel in a single cylinder direct injection diesel engine and found that the carbon
monoxide, smoke and NOX emissions were lower. Usta [91] conducted an experimental
study on exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester
and concluded that there is reduction in CO and SO2 emissions while causing slightly
increase in NOX emissions. Labeckas and Slavinskas [92] analyzed the emission
characteristics of four stroke, four-cylinder, direct injection, unmodified, naturally
aspirated diesel engine when operating on neat rapeseed methyl ester and its 5, 10, 20 and
35% blends with diesel fuel. They observed that CO, HC and visible emissions had
decreased while NOX emissions increased for methyl ester compared to diesel. The
control of NOX emission of biodiesel (rapeseed oil, linseed oil, rice bran oil, soybean oil)
was also investigated by Deepak et al. [93]. The use of hot exhaust gas recirculation for
oxides of nitrogen control in a compression ignition engine fuelled with jatropha
biodiesel was investigated by Pradeep and Sharma [94]. Sahoo et al. [31] reported that
polanga oil methyl ester showed lesser exhaust emission as compared to high-speed
diesel. Melissa et al. [95] investigated the two routes to reformulate soy-based biodiesel
in an effort to reduce nitrogen oxide emissions.

Several countries have active biodiesel programs, with European Union and
United States as the leaders. In order to promote biodiesel and help it to compete with
petroleum diesel, many countries have drawn up tax support packages. For example,
Germany and Italy levies no tax, UK has 20% lower tax and, several US states imposed
lower tax on fuels containing biodiesel. Edible oils like soybean and rapeseed are common feedstocks used for biodiesel production in USA and Europe.

Majority of Asian countries are net importer of edible oils, therefore these oils cannot be used for the production of biodiesel. In South Asian countries like India, biodiesel can be harvested and sourced from non-edible seed oils like jatropha and pongamia. Literature related to prospects of these oils as biodiesel production is discussed in next chapters.

1.9 ADVANTAGES OF BIODIESEL

Biodiesel is environmental friendly because of lower HC emissions, smoke and soot reductions, lower CO emissions, reduction of greenhouse gases. Biodiesel contains no sulphur. Biodiesel does not produce greenhouse effects, because the balance between the amount of CO₂ emissions and the amount of CO₂ absorbed by the plants producing vegetable oil is equal.

Biodiesel is biodegradable and renewable and can help reduce dependency on foreign oil. It helps to lubricate the engine itself, decreasing engine wear. Biodiesel can be used directly in compression ignition engines with no substantial modifications of the engine. B20 can be used without engine modifications. The cost of biodiesel, however, is the main obstacle to commercialization of the product. The viability of a continuous transesterification process and the recovery of high-quality glycerol as a biodiesel byproduct are primary options to be considered to lower the cost of biodiesel [16, 96].

1.10 DISADVANTAGES OF BIODIESEL

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher low temperature flow properties, higher NOₓ emissions, lower engine speed and power, injector coking, engine compatibility, and high price.

Oxidation stability (OS) is lower than that diesel so that under extended storage conditions it is possible to produce oxidation products that may be harmful to the vehicle
components. The oxidation of fatty acid chain is a complex process proceeded by a variety of mechanisms. Oxidation of biodiesel is due to the unsaturation in fatty acid chain and presence of double bonds in the molecule offers high level of reactivity with oxygen, especially, when it is placed in contact with air/water. The primary oxidation products of double bonds are unstable allylic hydroperoxides which are unstable and easily form a variety of secondary oxidation products [97]. This includes the rearrangement of product of similar molecular weights to give short chain aldehydes, acids compounds and high molecular weight materials.

**Table 1.6.** Influence of residual products of biodiesel on diesel engine [44, 98-101]

<table>
<thead>
<tr>
<th>Oxidation impact</th>
<th>Impact on fuel injection equipment</th>
<th>Influence on vehicle product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers, <em>Insoluble</em></td>
<td>• Filter clogging • Deposits formation inside FIE • Injector coking • Seizure of moving parts</td>
<td>• Poor performance, stalling • No start • Increased smoke • Filter clogging</td>
</tr>
<tr>
<td>Polymers, <em>Soluble</em></td>
<td>• Resins formed inside FIE • Form in soluble when blended with diesel</td>
<td>• Poor performance, stalling • No start</td>
</tr>
<tr>
<td>Total acid</td>
<td>• Corrosion of metal parts • Foam from soap formation with metal ions from wear or corrosion</td>
<td>• Poor performance, stalling • Increased smoke • No start • Corrosion of metal parts</td>
</tr>
</tbody>
</table>

All these make biodiesel relatively unstable on storage and residual products of biodiesel such as insoluble gums, total acids, and aldehydes formed from degradation may cause engine problems like filter clogging, injector coking, and corrosion of metal parts (Table 1.6) [44, 98-101]. This is why the OS is an important criterion for biodiesel. The biodiesel standards IS-15607 and EN-14214 call for determining oxidative stability at 110°C with a minimum induction period (IP) of 6h by the Rancimat method (EN-
Even ASTM standard D-6751 has recently introduced a minimum IP of 3h [100,101].

The research on biodiesel stability has been put on top priority by voting at Annual Biodiesel Technology Workshop held at Chicago on 12 and 13, January 2005 [102]. Different factors like air, extended storage etc. can influence the OS of biodiesel. No research is available on the influence of the presence of metals, commonly found in the metallurgy of biodiesel storage tanks and barrels; on the OS of biodiesel with the Rancimat test method.

Biodiesel has certain limitations at low temperatures. The low temperature flow properties of biodiesel are characterized by cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) and these must be considered when operating compression-ignition engines in moderate temperature climate during winter months. “CP” is the temperature at which a sample of the fuel starts to appear cloudy, indicating that wax crystals have begun to form which can clog fuel lines and filters in a vehicle’s fuel system, “PP” is the temperature below which the fuel will not flow, and “CFPP” is the temperature at which fuel causes a filter to plug as a result of its crystallization [103-106]. At these temperatures, there might be problem in engine running due to plugging of filters. Residual products like unused oil or fatty acid in transesterification process can effect these low temperature flow properties and other physico-chemical properties of biodiesel.
1.11 OBJECTIVES OF THE PRESENT WORK

A renewable fuel such as biodiesel, with lesser exhaust emissions, is the need of the day. Therefore, researchers and scientific community worldwide have focused on the development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially. Present research has following objectives:

1. Synthesis and physico-chemical evaluation of biodiesel from tree borne non-edible oil seeds.

2. To study OS of biodiesel from tree borne non-edible oil seeds by Rancimat test method and to study the impact of antioxidants on OS of biodiesel by doping with antioxidants.

3. To study the influence of different transition metals *viz.* iron, nickel, manganese, cobalt, and copper, commonly found in metallurgy of biodiesel storage tanks and barrels on biodiesel OS

4. To study the impact of antioxidants and metal deactivators respectively, on the metal-contaminated biodiesel.

5. To study the synergistic effect of metal deactivators and antioxidants on oxidation stability of metal-contaminated biodiesel

6. To study the influence of organic contaminants like water, soaps, glycerides etc. likely to be present in biodiesel, on the OS and physico-chemical properties like CP, PP and CFPP of biodiesel.

7. To improve the OS and physico-chemical properties of organic-contaminated biodiesel.

8. To establish the correlation between various physico-chemical properties of biodiesel.