CHAPTER 4

BIODIESEL - THEVETIA PERUVIANA SEED OIL

4.1 INTRODUCTION

Under Indian conditions plant varieties, which are non-edible and which can be grown abundantly in large-scale on wastelands, can be considered for biodiesel production. Some of the prominent non-edible oil seed producing plants include *jatropha curcas, pongamia pinnata, neem and rubberseed* etc. In this research work, biodiesel production from a new plant source called *Thevetia Peruviana* has been investigated.

4.2 SELECTION OF SPECIES: THEVETIA PERUVIANA

Considering all options available among non-edible tree-bearing oil seeds, *Thevetia Peruviana* has been identified as one of the most suitable seeds. It grows practically all over India under a variety of agro-climatic conditions. Thus it ensures a reasonable production of seeds with very little inputs.

*Thevetia Peruviana*, called *Manjarali* in Tamil Nadu, is a small evergreen tree (3-4 m high) cultivated as an ornamental plant in tropical and subtropical regions of the world, including India. Fruit contains 2-4 flat gray seeds, which yield about half a litre of oil from one kg of dry kernel. *Thevetia Peruviana* plant and flower are shown in Figures 4.1 and 4.2 respectively. This plant can be cultivated in wastelands. It requires minimum water when it
is in growing stage. It starts flowering after one and a half year. After that, it blooms thrice every year. Figures 4.3 and 4.4 show the *Thevetia Peruviana* fruit and seed as well as kernels.

**Figure 4.1** *Thevetia Peruviana* plant with fruit

**Figure 4.2** *Thevetia Peruviana* flower
Figure 4.3 *Thevetia Peruviana* fruits

Figure 4.4 *Thevetia Peruviana* seed and kernels

4.3 *THEVETIA PERUVIANA*: PREFERRED OPTION

The advantages of the species are as follows:

- *Thevetia Peruviana* can be grown in arid zones as well as in higher rainfall zones and even on land with thin soil cover.
- It can be a good plantation material for eco-restoration in all types of wasteland.
- It grows readily from plant cuttings or seeds up to the height of 3-4 m.
- The plant removes carbon from the atmosphere, stores it in the woody tissues and assists in the build up of soil carbon.

4.4 **THEVETIA PERUVIANA: LIMITATIONS**

The *Thevetia Peruviana* also suffers from certain limiting factors, which need to be kept in mind while dealing with it. These are as follows:

- *Thevetia Peruviana* can not be grown on water-logged lands.
- *Thevetia Peruviana* seeds are highly toxic.

4.5 **THEVETIA PERUVIANA CULTIVATION: YIELD AND PRODUCTIVITY**

India being an agriculture-based country, cultivating crops for vegetable oil will not be a big problem. It is estimated that 7 million acres of plantation is required to produce 10% replacement of petrodiesel need in India. According to economic survey of government of India, out of cultivated land area, about 175 million hectares are classified as waste degraded land which can be easily used for plantation of oil seed plants.

Apart from planting seeds, *Thevetia Peruviana* can also be propagated from cuttings. Use of branch cutting for propagation results in rapid growth and the bush can be expected to bear fruit within one and a half
year. The planting pitch could be $2m \times 2m$ thus resulting 2500 plants per hectare. Wider spacing gives larger yields of fruit.

_Thevetia Peruviana_ can bloom and produce fruit thrice in a year. To withstand extreme drought conditions, _Thevetia Peruviana_ plant sheds leaves to conserve moisture, which results in reduced growth. Although _Thevetia Peruviana_ is adapted to soils with low fertility and alkalinity, better yields can be obtained on poor quality soils if fertilized. _Thevetia Peruviana_ plant yield stabilizes from 3rd and 4th year onwards. The plant has an average life with effective yield of more than 50 years.

The cost of plantation has been estimated as Rs.20,000/- per hectare, inclusive of plant material, maintenance for one year, training, overheads etc.,. It includes elements such as site preparation, digging of pits, fertilizers, irrigation and deweeding and plant protection for one year i.e., the stage when it will start bearing fruits.

### 4.6 EXTRACTION OF _THEVETIA PERUVIANA_ SEED OIL

Figure 4.5 shows the operations involved in extraction of TPSO. While collection of fruits and removing flesh from the fruit for collection of seed, wearing glouse is essential; Because the entire parts of the plan is milky nature.

#### 4.6.1 Preparation of Seeds

The ripe fruits are plucked from the trees and seeds are sun dried. They are decorticated manually. The oil from _Thevetia Peruviana_ seeds can be extracted by mechanical extraction using a screw press.
4.6.2 Purification of Oil

The oil extracted is purified by sedimentation technique. This is the easiest way to get clear oil, but it takes about a week until sediments settle down.
4.6.3 Processing of Oil

The important factors to be considered for biodiesel production process include:

- Possibility of processing of vegetable oil without or minimum modification.
- Possibility of processing free fatty acid containing oils/feed stocks.
- Process should be environment friendly with almost zero effluent.

The selection of appropriate technology for production of biodiesel calls for careful selection of processing steps, catalyst and downstream process integration.

4.7 VISCOSITY REDUCTION TECHNIQUES

High viscosity of vegetable oils has been reported by almost all researchers (Selim Centinkaya et al (2001); Senthil Kumar et al (2001); Naveen Kumar and Dhuwe (2004)) as the major bottleneck in their use as fuel. To overcome this problem, various techniques have been successfully tried and the advances in this area are summarized below.

4.7.1 Preheating

High viscosity is a major problem with vegetable oil in using it as engine fuel; one possible solution is to heat the oil in order to reduce its viscosity or to heat the intake air in order to accelerate the evaporation of the vegetable oil in the engine (Deepak Agarwal and Avinash Kumar Agarwal 2007).
4.7.2 Blending

Vegetable oil can be directly mixed with diesel fuel and may be used for running an engine. The blending of vegetable oil with diesel fuel has been investigated by several researchers. It has been proved that the use of 100% vegetable was also possible with some minor modifications in the fuel system (Pereira et al 2007; Ramadhas et al 2008; Nico Samec et al 2002).

4.7.3 Micro-emulsification

The formation of micro-emulsion (co-solvency) is one of the potential solutions in solving the problems of vegetable oils viscosity. Micro-emulsion is defined as transparent, thermodynamically stable colloidal dispersions. The droplets diameters in micro-emulsions range from 100-1000 Å. A micro-emulsion is made of vegetable oils with ester and dispersant (co-solvent), or of vegetable oils, or an alcohol and a surfactant and a cetane improver, with or without diesel fuels (Niko Samec et al 2002).

4.7.4 Cracking/Pyrolysis

Cracking is the process of conversion of one substance into another by means of heat or with the aid of catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl ester of fatty acids. The pyrolyzate has lower viscosity, flash and pour point than diesel fuel but equivalent calorific value. The cetane number of the pyrolyzate is lower.
Transesterification is a most commonly used and an important method to reduce the viscosity of vegetable oils. In this process triglyceride reacts with three molecules of alcohol in the presence of a catalyst producing a mixture of fatty acids, alkyl ester and glycerol. The process of removal of all the glycerol and the fatty acids from the vegetable oil in the presence of a catalyst is called esterification (Vedararaman et al 2005a). This esterified vegetable oil is called bio-diesel. Biodiesel properties are similar to diesel fuel. It is renewable, non-toxic, biodegradable and environment friendly transportation fuel. After esterification of the vegetable oil its density, viscosity, cetane number, calorific value, atomization and vaporization rate, molecular weight, and fuel spray penetration distance are improved more. So these improved properties give good performance in CI engine.

Physical and chemical properties are improved in esterified vegetable oil because esterified vegetable oil has a higher cetane number than straight vegetable oil. These parameters induce good combustion characteristics in vegetable oil esters. So unburnt hydrocarbon level is decreased in the exhaust. It results in lower generation of hydrocarbon and carbon monoxide in the exhaust than diesel fuel. The vegetable oil esters contain more oxygen and lower calorific value than diesel. So, it enhances the combustion process and generates lower nitric oxide formation in the exhaust than diesel fuel.

In addition to the above methods, supercritical method is also found to reduce the viscosity of oil (Balat 2008; Saka and Kusdiana 2001). This method is so easy to convert vegetable oil into biodiesel.
4.8 CHEMISTRY OF TRANSESTERIFICATION

Transesterification is the process of using an alcohol (e.g. methanol or ethanol) in the presence of catalyst, such as sodium hydroxide (NaOH) or sodium methoxide (NaOMe) or Potassium hydroxide (KOH), to chemically break the molecule of the raw renewable oil into methyl or ethyl esters with glycerol as a by product.

4.8.1 Chemical Structure of Transesterification

\[
\begin{align*}
\text{CH}_2\text{OOOCR} & \quad \text{CH}_2\text{OH} \\
| & \\
\text{CHOOCR} + 3\text{CH}_3\text{OH} \rightarrow & 3\text{CH}_3\text{OOOCR} + \text{CHOH} \\
| & \quad \text{(Catalyst NaOH)} \\
\text{CH}_2\text{OOOCR} & \quad \text{CH}_2\text{OH} \\
\text{Triglyceride} & \quad \text{Methanol} \\
\text{Methyl Esters} & \quad \text{Glycerol} \\
\text{Glycerin} & \quad \text{Fatty Acid I} \\
\quad & \quad \text{Fatty Acid II} \\
\quad & \quad \text{Fatty Acid III}
\end{align*}
\]

Transesterification

1 mole Triglyceride + 3 mol Methanol + Catalyst \(\rightarrow\) 3 mol Methyl ester + 1 mol Glycerin + Catalyst.
### 4.8.2 Benefits of Transesterification

1. Reduces viscosity of the oil
2. Increases the volatility
3. Improves cetane number
4. Reduces sulphur and aromatics
5. Improves emission with oxidation catalysts
6. Improves oxygen content (11%)
7. Improves lubricity
8. Improves winter operability (-22°C)

### 4.9 TRANSESTERIFICATION PROCESS SETUP

The setup (Figure 4.6) in which the methyl ester of TPSO was prepared consists of the following components.

- Round bottle flask
- Condenser
- Magnetic stirrer/Paddle
- Dimmer start
- Thermometer
- Measuring jars
- Separating funnel
Figure 4.6 Transesterification setup

Openings are provided in the round bottom flask for connecting condenser and temperature sensor. The heater coil surrounds the reactor vessel and it provides uniform heating all round the flask. The magnetic stirrer enables proper mixing of the TPSO and methanol. The speed of the stirrer is adjustable. Dimmer start is used to control the voltage so that constant temperature can be maintained. Condenser is used to condense alcohol if it vaporizes from the mixture. Separating funnel helps to separate biodiesel from glycerol.

4.10 MAKING OF BIODIESEL FROM TPSO

- Materials used
  - Raw TPSO
  - Methanol
  - Sodium hydroxide
  - Petroleum ether
  - Distilled water
Initially to start the experiment

- 100 grams of raw TPSO.
- Required quantity of 15% by vol. of methanol.
- Required amount of sodium hydroxide (NaOH) (i.e. 6% of catalyst) are taken as inputs.

First methanol (CH$_3$OH) and accurately weighed sodium hydroxide (NaOH) (Catalyst) are mixed vigorously for 10-15 minutes. Then the sodium methoxide formed is mixed with the moisture free TPSO in round bottom flask. The magnetic stirrer and heating are switched ON. The speed of the magnetic stirrer is maintained at constant value. The temperature of the reactant is maintained at the required reaction Temperature. The dimmer start should be properly adjusted to control the voltage and thereby maintaining the temperature at 55-60°C.

Once the reaction time is over, the contents are emptied into a separating funnel. If the reaction is complete, two layers will be formed within few minutes. For proper separation, it should be allowed to settle for two to four hours. A thick yellow high viscous glycerol layer at the lower phase of the funnel can be seen. The methyl ester of TPSO at the upper phase of the funnel can be seen. The methyl ester is washed with water, petroleum ether and neutralized with water. Translucent methyl ester of TPSO is named as biodiesel (METPSO). The transesterification flow process for biodiesel production is indicated in Figure 4.7.
PROPERTIES OF TEST FUEL

The properties of test fuel such as calorific value, specific gravity, kinematic viscosity, cetane number and different temperature (Flash point, Fire point, Cloud point, Pour point) are found, which are listed in Table 4.1.
Table 4.1 Properties of fuels used

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel</th>
<th>TPSO</th>
<th>METPSO</th>
<th>B20</th>
<th>ASTM code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorific value, kJ/kg</td>
<td>43200</td>
<td>40148</td>
<td>40462</td>
<td>42652</td>
<td>D4809</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.804</td>
<td>0.92</td>
<td>0.839</td>
<td>0.811</td>
<td>D445</td>
</tr>
<tr>
<td>Kinematic viscosity (at 40°C)cSt</td>
<td>3.9</td>
<td>38</td>
<td>4.2</td>
<td>3.96</td>
<td>D2217</td>
</tr>
<tr>
<td>Cetane number</td>
<td>46</td>
<td>42</td>
<td>49</td>
<td>48</td>
<td>D4737</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>56</td>
<td>158</td>
<td>110</td>
<td>72</td>
<td>D92</td>
</tr>
<tr>
<td>Fire point, °C</td>
<td>64</td>
<td>165</td>
<td>120</td>
<td>79</td>
<td>D92</td>
</tr>
<tr>
<td>Cloud point, °C</td>
<td>-8</td>
<td>2</td>
<td>-4</td>
<td>-7</td>
<td>D97</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>-20</td>
<td>-5</td>
<td>-10</td>
<td>-12</td>
<td>D97</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>0.001</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
<td>D976</td>
</tr>
</tbody>
</table>

4.12 CHARACTERIZATION OF BIODIESEL

The following are the important characteristics of good vegetable oil required to substitute diesel fuel.

4.12.1 Ignition Quality

Satisfactory combustion demands self-ignition of the fuel as it is sprayed near TDC into the hot swirling compressed cylinder gas. Long ignition delay is not acceptable as it leads to knock. Therefore, the cetane number of the substitute fuel should be high enough, which is a measure of knock tendency of the fuel. Satisfactory fuels must have a cetane number between 40 and 60.

4.12.2 Viscosity

Fuel viscosity plays an important role in combustion. The direct injection in the open combustion chamber through the nozzle and pattern of
fuel spray decides the ease of combustion and thermal efficiency of the engine. Too low a viscosity can lead to excessive internal pump leakage and the system pressure will reach an unacceptable level and will affect injection during the spray atomization. The effect of viscosity is critical at low speed or light load conditions.

4.12.3 Heating Value

Although the diesel combustion chamber system can accept fuels with wide variations in heating value, it is better suited for fuels with higher calorific value. This helps to reduce the quality of fuel handled and maximizes the equipment operating range. It is always desirable for the vegetable oil to have a calorific value nearer to that of diesel.

4.12.4 Important Temperature

Pour point and cloud point are important for cold weather operations of the IC engine. For satisfactory working, the values of both should be well below the freezing point of the oil used.

Flash point is an important temperature from a safety point of view. This temperature should be as high as possible and its typical values for commercial vegetable oils range between 50 and 110°C.

4.12.5 Other Properties

The sulphur content, carbon residue and ash are responsible for corrosion and forming a residue on the engine parts which will affect the engine life. These values should be as small as possible. Practical values are 0.5% sulphur, 0.27% carbon residue and 0.01% ash.