CHAPTER III

MATERIALS AND METHODS

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3.1 Study Site

The site selected for collecting the oil seeds were the forests of the state of Assam, located in the north-east India. The state is located between 24°8’ to 28°9’ N latitude and 89°42’ to 95°16’ E longitude. It experiences a humid subtropical climate with an average rainfall ranging from slightly below 1400mm to slightly above 3000mm. The mean maximum temperature goes upto 37° C in summer and mean minimum temperature comes down to10° C in winter. Soils of the state are slightly acidic in nature.

3.2 Selection of the oil seeds

In the forests of north-east India a variety of indigenous oil seeds bearing plants grow well in their natural habitats. For the present study we selected the oil seeds of *Mesua ferrea* L. and *Pongamia glabra* Vent. trees. These two trees are found in abundance in this region and their seeds contain high percentages of oil which are nonedible. At present the seeds of these trees are not utilized for any productive purpose.

3.3 Characteristics of the tree species

Characteristics of *Mesua ferrea* and *Pongamia glabra* on the basis of their botanical description, wood quality, availability etc. are described elsewhere (Hooker, 1875; Dutta, 1985).

*Mesua ferrea*

- Botanical Name: *Mesua ferrea* L.
- English Name: Iron wood tree
Vernacular Name: Nahar (Assamese); Nageswar (Hindi).

Family: guttiferae

It is a middle-size tree that grows mostly in the mountains of the Eastern Himalayas, Eastern Bengal, Eastern and Western Peninsulas and Andaman.
Islands. In Assam it is found particularly in upper Assam, lower Nagaland, Darrang district and the North Cashar Hills. Its seeds contain 75% percent of oil on the basis of shelled kernel weight. Flowering starts in April-May and seeds become mature in August-October. A fully mature tree yields 30-60 kg of seeds annually. *Mesua ferrea* is one of the hardest trees of north-east India. Its timbers are used in railway sleepers, construction of houses, furniture and cart wheels etc. In early days when kerosene and electricity were not available the rural people of this region used its seeds for illumination at night. Flowers and leaves have snake repellant properties.

**Pongamia glabra**

| Botanical Name | : *Pongamia glabra* Vent. |
| English Name | : Indian Beech, Pongam, Hongay. |
| Vernacular Name | : Koroch (Assamese), Papar (Hindi). |
| Family | : Leguminosae |

Fig. 8. *Pongamia glabra* Vent. tree

Fig. 9. *Pongamia glabra* seeds and their kernels

It is a middle-size evergreen tree with spreading branches. In north-east India it is normally found in Lakhimpur, Sibsagar, Dibrugarh, Darrang, Kamrup and Nowgong
districts of Assam, lower Nagaland and Meghalaya. Wood of *Pongamia glabra* is hard and heavy and yellowish in colour. A fully mature tree yields 20-50 kg of seeds yearly. The oil content of the seeds varies from 30-35%. The oil is used in treatment of skin disease and fresh bark is used as medicine in the treatment of piles.

### 3.4 Extraction of oils:

About 100 kg of *Mesua ferrea* seeds were collected from mature trees grown in the forests of Assam in October 2004 and dried at 50°C for 24h in a hot air oven. The dried seeds were shelled and milled. The oil was extracted from the milled kernels with petroleum ether (40-60 °C) using the Soxhlet extraction method (Raheman and Phadatare, 2004). The solvent was removed from the extract and the oil content was found to be 75% by weight of the milled kernel. About 10 litres of the oil were extracted and kept over anhydrous sodium sulphate for three days and filtered through glass wool to remove the particulate matter present in it. The filtered oil was then stored in glass bottles for further experiments.

About 100 kg of the *Pongamia glabra* seeds were collected from the forest of Assam in March 2004 and dried at 50°C for 24h. The dried seeds were shelled and milled. About 10 lit of the oil were extracted from the milled kernels through a similar procedure used for extraction of oil from *Mesua ferrea* seeds. The oil content was found to be 33.6% by weight of the milled kernel. The extracted oil was kept over anhydrous sodium sulphate for three days and then filtered through glass wool. The filtered oil was then stored in glass bottles for further experiments.

### 3.5 Determination of the properties of the oils:

Various properties such as density, pour point, kinematic viscosity, acid value, ash content, carbon residue, calorific value etc. of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined by different standard methods.

Density was determined by ASTM D287 method.

Pour point was determined by ASTM D97 method.
Kinematic viscosity at 40° C was determined by ASTM D445 method.

Acid value was determined by ASTM D874 method.

Carbon residue was determined by ASTM D4530 method.

Calorific value was determined by using a bomb calorimeter.

All the tests were carried out in triplicate and average values are presented in Tables 4 & 5.

3.6 Determination of fatty acid composition of the oils:

Fatty acid composition of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined by using a GC as per AOCS official method 1998, Ce 1-62 and Ce 2-26. GC analysis was carried out in triplicate and the average values are presented in Table 4 & 5.

3.7 Production of Biodiesel from *Pongamia glabra* seed oil:

The production of biodiesel (methyl ester) of *Pongamia glabra* seed oil was carried out in a 2lit. capacity glass vessel equipped with a mechanical stirrer, a funnel and a condenser placed in water bath having a proportional integral derivative temperature control device. *Pongamia glabra* seed oil (500ml) and 150 ml of methanol (98% pure) were mixed (1:6 molar ratio) and the mixture was placed inside the reactor. The temperature of the reactor was raised to 60° C, and the mixer was stirred at 600rpm. When the mixture temperature reached 60° C, 4.5g of freshly prepared sodium methoxide was added to it. Thus the reaction was continued for 1h, an optimum reaction time, as determined from three sets of experiments conducted initially for 0.5, 1, and 1.5 h duration. As soon as the reaction time was over, the mixture was placed in a separating funnel and allowed to cool for 2h. Two distinct layers were found to form, the upper layer being the mixture of methyl ester and unreacted methanol and the lower layer was a mixture of glycerol and water. A rotary vacuum evaporator was used to recover the unreacted alcohol from the ester layer. The unreacted alcohol recovered was found to be 30ml. The ester was then washed twice with distilled water. The emulsified water was removed through rotary vacuum evaporator method. Biodiesel (488ml) and
32 ml of glycerol were recovered by this method. A small quantity of the esters thus produced was kept separately for Sim-Dis distillation in a gas chromatograph. The remaining esters were then refined by distilling under reduced pressure. Following the same procedure a 10 lit. of biodiesel from *Pongamia glabra* seed oil was produced and kept over anhydrous sodium sulphate for further experiments.

![Pongamia glabra seed oil](image1)

Fig. 10. *Pongamia glabra* seed oil

![Mesua ferrea L. seed oil](image2)

Fig. 11. *Mesua ferrea* L seed oil

![Refined biodiesel from Pongamia glabra seed oil](image3)

Fig. 12. Refined biodiesel from *Pongamia glabra* seed oil.

![Refined biodiesel from Mesua ferrea L. seed oil](image4)

Fig. 13. Refined biodiesel from *Mesua ferrea* seed oil.
3.8 Production of Biodiesel from *Mesua ferrea* seed oil:

Following the same procedure and the same reactor as used in the production of biodiesel from *Pongamia glabra* seed oil and using sodium methoxide catalyst, we attempted to produce biodiesel from *Mesua ferrea* seed oil using sodium methoxide catalyst. It was observed that the yield of biodiesel was quite low (< 85%) and the separation of the ester layer from glycerol layer was found to be very difficult. Canakci and Van Gerpen (1999) has suggested that special processes are required for transesterification of oil or fat containing significant amount of free fatty acids (FFAs). They reported that pretreatment processes using strong acid catalyst have been shown to provide good conversion yields and high quality final products. Hence for production of biodiesel from *Mesua ferrea* seed oil which contains higher amounts of free fatty acids (Acid value, 16.4mg KOH/g), we attempted to produce biodiesel through a two step process. In the first step esterification of the free fatty acids to methyl esters was carried out using sulphuric acid catalyst. In the second step low free fatty acids pretreated oil was esterified with alkali catalyst to convert to methyl esters. Keim (1945) used this method to convert palm oil containing 50.8% of free fatty acids to methyl esters.

**Experimental procedure**

A 500 ml of *Mesua ferrea* seed oil and 150ml of methanol (98% pure) were mixed (1:6 molar ratio) and the mixture was placed inside a 2lit capacity glass reactor. A 5ml of conc. sulphuric acid was then added to the mixture. The temperature of the reactor was raised to 60°C and the mixture was stirred at 600 rpm for 1.5 h. As soon as the reaction was over, the mixture was placed in a separating funnel. After cooling, the upper layer being the mixture of esters, unreacted triglycerids and unreacted methanol was separated from the lower layer. After neutralization of this mixture with KOH solution, 1.25% sodium methoxide was added, and the mixture was stirred for an additional 1h at 60°C. The mixture was then placed in a separating funnel where two distinct layers were found to form. The upper layer was the mixture of esters and the unreacted methanol while the lower layer consisted of salt, water and glycerol. The
esters were then separated from methanol through rotary vacuum evaporation method. A small quantity of the esters thus produced was kept separately for Sim-Dis distillation in a gas chromatograph. The remaining esters were then refined by distilling under reduced pressure. The yield of esters thus produced was 94%. Thus about 10 lit. of biodiesel were prepared and stored in glass bottles for further experiments.

3.9 Determination of Properties of the Biodiesels

Various properties of the biodiesels thus obtained from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined by different standard test methods.

- Density was determined by ASTM D 287 methods.
- Ash content was determined by ASTM D 874 method.
- Carbon residue was determined by ASTM D 4530 method.
- Pour point was determined by ASTM D 97 method.
- Flash point was determined by ASTM D 93 method.
- Water content was determined by ASTM D 2709 method.
- Kinematic Viscosity at 40\(^\circ\) C was determined by ASTM D 445 method.
- Cetane number was determined by ASTM 613 method (in CFR cetane).
- Acid value was determined by ASTM D 664 method.
- Sulphur content was determined by ASTM D 5453 method.
- Oxidation stability test was done by ASTM D 2274 method.
- Initial boiling point (IBP) and final boiling point (FBP) were determined by Sim-Dis GC distillation (ASTM D 2887 and D86 correlation).
- Calorific values were determined by using an Adiabatic Bomb calorimeter.

All the tests were carried out in triplicate and the average values are reported in Tables-7 & 8.

3.10 Preparation of biodiesel blends with petroleum diesel

A 100 lit. petroleum diesel used in blending with the biodiesel was obtained from Numaligarh Refinery Limited, Assam. Specifications of the petroleum diesel are given in Table 9.
Five different blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel were prepared in the following compositions.

**B5**: 5% (vol.) of biodiesel + 95% (vol.) of petroleum diesel.

**B10**: 10% (vol.) of biodiesel + 90% (vol.) of petroleum diesel.

**B15**: 15% (vol.) of biodiesel + 85% (vol.) of petroleum diesel.

**B20**: 20% (vol.) of biodiesel + 80% (vol.) of petroleum diesel.

**B25**: 25% (vol.) of biodiesel + 75% (vol.) of petroleum diesel.

Similarly, five different blends of biodiesel from *Pongamia glabra* seed oil with petroleum diesel were prepared in the following compositions

**B10**: 10% (vol.) of biodiesel + 90% (vol.) of petroleum diesel.

**B20**: 20% (vol.) of biodiesel + 80% (vol.) of petroleum diesel.

**B30**: 30% (vol.) of biodiesel + 70% (vol.) of petroleum diesel.

**B40**: 40% (vol.) of biodiesel + 60% (vol.) of petroleum diesel.

**B50**: 50% (vol.) of biodiesel + 50% (vol.) of petroleum diesel.

Since the viscosity of *Pongamia glabra* biodiesel was found to be lower than *Mesua ferrea* biodiesel, we prepared the blends of *Pongamia glabra* biodiesel starting from 10% (vol.) of it.

### 3.11 Determination of properties of the biodiesel blends with petroleum diesel

Various properties of the blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel and biodiesel from *Pongamia glabra* seed oil with petroleum diesel, thus prepared were determined by using different standard methods as used in the case of neat biodiesel of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil. All the tests were carried out in triplicate and the average values are reported in Tables 13 & 14.

### 3.12 Diesel engine performance and emission tests

Diesel engine performance tests and emission characteristics of two selected biodiesel blends namely B5 and B20 and also the typical petroleum diesel were carried out in a Bajaj-Tempo, direct injection, 4 cylinder, 4 stroke, vertical, water cooled
computer-based Test IC diesel engine. Technical details of the diesel engine are given in Table 3.

Table 3:- Technical details of the diesel engine.

<table>
<thead>
<tr>
<th>Type of engine</th>
<th>Bajaj-Tempo, direct injection, 4-cylinder, 4-stroke, vertical, water-cooled, computer-based Test IC diesel engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rated output</td>
<td>34 kW at 3800 RPM</td>
</tr>
<tr>
<td>Bore</td>
<td>78 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>94 mm</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>19.8 : 1</td>
</tr>
<tr>
<td>Capacity</td>
<td>1797 cm$^3$</td>
</tr>
<tr>
<td>Throttle opening</td>
<td>100 %</td>
</tr>
<tr>
<td>Maximum cylinder volume</td>
<td>450 cm$^3$</td>
</tr>
<tr>
<td>RPM, Dynamometer load (kg)</td>
<td>3500 ± 10, 39 ± 0.15; 3000 ± 10, 43 ± 0.15; 2500 ± 10, 44 ± 0.15.</td>
</tr>
</tbody>
</table>

For each of the fuels under test, the engine was set for 0.5h, without applying load and then load was applied at 2500, 3000 and 3500 rpm engine speed. All the required data were recorded automatically in a computer coupled with both the engine system and the dynamometer.

Emission characteristics of CO and NOx were measured with the help of a smokemeter and a portable NUCON series 400 toxic gas analyzer.

Sim-Dis GC distillations of the biodiesels and the petroleum diesel were carried out at Numaligarh Refinery Laboratory.