Development Of Biodiesel from the Oil of Garcinia Gummigutta (Sour Garcinia) by Transesterification

Abstract— The Garcinia gummigutta trees are widely available and grow in tropical regions of Asia and Africa. The Garcinia trees are indigenous to India grow in deciduous and semi evergreen forests of southern Western Ghats of India. The seeds fallen are collected and oil is extracted at village level expellers. Growing Garcinia trees would also help in protecting the environment and benefit the farmers as well. The biodiesel produced by the oil of Garcinia is considered as one of the best substitute for diesel. FFA test is conducted using titration method. As the raw oil consists of high viscosity and free fatty acid (FFA) the three stage standard transesterification method is used to produce biodiesel. The stage wise transesterification removes impurities, wax, gums, etc and the tri glycerides are converted into methyl esters and glycerine. The neat biodiesel is obtained after the removal of glycerine and water wash. Increase in awareness and growth in research in this area can motivate Garcinia gummigutta as the alternative source of fuel by replacing diesel. In the present study attempt has been made to develop the biodiesel from the oil of Garcinia gummigutta.

Key words— Garcinia gummigutta,free fatty acid, transesterification, catalyst, titration, biodiesel, methyl esters.

I. INTRODUCTION

Energy is a basic need of human kind like food and shelter . Increase in population, industrial growth and living standard of people develop the impact on conventional resources. On the other hand depleting nature of fossil fuels and emissions released by fossil fuels limits the use of them. Production of biodiesel from oil and ethanol from sugar based resources are considered as the best substitute of diesel and gasoline respectively in the country. Vegetable oil as an alternative fuel has been under study at the University of Idaho since 1979. Use of vegetable oil in diesel engines is not a radically new concept as the inventor of diesel engine “Rudolf Diesel” demonstrated his first diesel engine at the World Exhibition at Paris in 1900 by using peanut oil as fuel. However due to abundant supply of petro-diesel, R&D activities on vegetable oil were not seriously pursued. Vegetable oils have comparable energy density, cetane number, heat of vaporization, and stoichiometric air/fuel ratio with mineral diesel fuel. But high viscosity of vegetable oils causes poor fuel atomization, large droplet size and thus high spray jet penetration causing operational problems related to starting ability, ignition, combustion and performance and durability problems related to deposit formation, carbonization of injector tip, ring sticking and lubricating oil dilution. (1,2,3,4)

II. VEGETABLE OILS AS A SOURCES OF BIODIESEL

Vegetable oils are generally composed of triglycerides whose molecular structures are branched and complex. The large molecular sizes of the component triglycerides result in the oils having higher viscosity compared with that of mineral diesel fuel. Due to the presence of double bonds in the molecular structure of vegetable oils, they can be modified easily as per requirement by treating with alcohols. Methyl or ethyl ester of fatty acid which is known as biodiesel is made from vegetable oils by the method known as transesterification.

Many researchers earlier produced the biodiesel from various vegetable oils. Oils from rapeseed, soyabean, sunflower, mahua, jatropha, neem, and pongamia oils have been successfully converted into biodiesel by transesterification using methanol or ethanol to study the physico chemical properties, performance and emission characteristics in IC engines using biodiesels. Amongst the many species, which can yield oil as a source of energy in the form of bio-fuel (5 to14)

III. GARCINIA GUMMIGUTTA AS SOURCE OF BIODIESEL

Amongst the many species, which can yield oil as a source of energy in the form of bio-fuel, “Garcinia gummigutta” locally known as Sour Garcinia has been found to be one of the most suitable species in India being grown. Garcinia gummigutta is the scientific name of commonly known Sour garcinia that belongs to the family of Clusiaceae. (16). It is also known as Camboge or Malabar tamarind, Found commonly in the evergreen forests of Western Ghats, from Konkan south to Travancore and in the Shola forests of Nigeria up to an altitude of 6000 ft. It flowers in November-February, and fruits ripen in April-May. Fruits are in June-July. The seeds of the fruit have edible fat, commercially known as Kokam butter. Kokum butter is considered nutritive, demulcent, astringent and emollient. It is suitable for ointments, suppositories. (15,16).The present study has been focussed on the...
development of biodiesel from the oil of Garcinia gummigutta (17,18,19,20)

IV. GARCINIA OIL EXTRACTION

Garcinia oil can be extracted from seed mainly by three methods. They are as follows

- Boiling method
- Expeller method
- Solvent extraction method

4.1 Extraction of oil by boiling conventional method

The finely dried and crushed seeds are then put in boiling water heated at 70 to 80°C and the mixture is stirred till the ghee floats on upper layer than separation of the ghee. The separation after boiling process and pre-treatment happens by gravity oil is mixed with hot water. Oil as lightest phase floats on hot water whereas the heavier residual waste at the bottom. The liquid fraction contains oil and water, which are further separated by heating so that water content evaporates from the oil. After the oil is separated, it is fed into the biodiesel processor to produce bio-fuel. Due to this process 5 to 10% of oil as to be extracted from one kg of Garcinia seeds.

4.2 Extraction of oil by expeller method

Sour Garcinia oil is extracted from the Sour Garcinia seeds through a mechanical expeller process. By this process 40% of oil could be extracted from one kg of Sour Garcinia seeds from this process.

4.3 Extraction of oil by solvent extraction method

Here the oil is extracted from seeds by using solvent, generally hexane, methanol, etc. From this process 25 to 30% of oil as to be extracted from one kg of Sour Garcinia seeds. (20)

V. TRANSESTERIFICATION

Transesterification is otherwise known as alcoholysis. It is the reaction of fat or oil with an alcohol to form esters and glycerin. A catalyst is used to improve the reaction rate and yield [2].In transesterification which is a popular conditioning of vegetable oil of present practice, one ester is converted into another. The reaction is catalyzed by either acid or base involving reaction with an alcohol, typically methanol if a bio-fuel is the desired product. This section deals with steps involved in the preparation of Biodiesel from untreated vegetable oils. A stoichiometric material balance yields the following simplified equation.

Fat or oil + 3 Methanol $\rightarrow$ 3 Methyl esters + Glycerol

The chemical reaction involved in this process is shown below.

\[
\begin{align*}
\text{R-COOCH}_3 + 3\text{CH}_3\text{OH} & \rightarrow 3\text{CH}_3\text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{C}_2\text{H}_5\text{O} \\
\text{R-COOH} + 3\text{CH}_3\text{OH} & \rightarrow 3\text{CH}_3\text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{C}_2\text{H}_5\text{O} \\
\end{align*}
\]

Say R = C18 H36 O2 for honge oil and R = C17 H34 O2 for mahua oil.

The reaction is catalyzed by either acid or base involving reaction with an alcohol, typically methanol if a bio-fuel is the desired product. [3,4,21].

5.1 Determination of free fatty acid in the oil

The standard titration method is used to calculate the FFA present in the oil.NaOH(0.1N) prepared using distilled water and NaOH pellets is taken in a burette.Calculated quantity of Gacinia oil and isopropyl alcohol is added in a clean and dry 250 ml conical flask.Few drops of NaOH(0.1N) is added and shaken well and the mixture is heated to about 60°C. Few drops of phenolphthalein indicator is added to this mixture.The titration process is carried out by drop by drop addition of NaOH(0.1N) from the burette into the mixture in the conical flask, mixing vigorously until a pink faint colour is obtained.The titration is stopped and the burette reading is noted down to calculate FFA as below.

\[
\text{Titratoin value}= 43.5 \text{ ml} \\
\text{FFA}=28.2\times(\text{Normality of NaOH})\times(\text{Titratoin Value})/\text{weight of oil} \\
\text{FFA}= 28.5\times0.1\times15/10=12\%.
\]

Fig1: Preparation of 0.1 N H2SO4
5.2 Three Stage: Trans-Esterification Process

Experimental Trans-esterification setup:

The experimental setup consists of 3-neck flask with magnetic stirrer and the condenser is fitted to the central neck as shown in the figure 3.

As the FFA present in the Garcinia oil is 12%, as the Trans-esterification process is carried in 3 stages.

5.2.1 Mild acid catalyzed transesterification

In first stage the raw oil is reacted with methanol in presence of orthophosphoric acid in order to neutralize the PH value of sour garcinia oil. The first stage removes organic matter and other impurities present in the oil in the presence of orthophosphoric acid, used as a reagent sour garcinia oil containing the impurities in considerable quantity and causes the transesterification difficulty. Hence, this necessitated the use of first stage. This is a type of reaction that takes place in the presence of methanol and orthophosphoric acid, helps in the separation of impurities which were dissolved in the methanol as an upper layer and oil in the lower layer.

5.2.2 Strong acid catalyzed transesterification

In second stage the sour garcinia oil is allowed to react with methanol in presence of H2SO4 in order to remove free fatty acid from sour garcinia oil. In this stage 1 litre of sour garcinia oil is taken into strong acid and 150ml of methanol and calculated quantity of concentrated H2SO4 around 3ml is added to the oil in the flask. And whole set up is kept ready. Then the mixture is kept agitated and heated in the reaction vessel (3-neck flask) at 60°C for 1hr30min. A dark layer was observed at the top layer of the oil. The mixture is then transferred to conical shaped separating funnel and allowed to settle at atleast 2 to 3 hours as shown in the figure 4. The black acid layer rises up and the bottom acid transesterified oil is drained back into the 3-neck flask to separate the glycerol.

5.2.3 Base catalyzed transesterification

In third stage transesterification process is done to reduce the complex chain into simplex long chain of ester. In this stage the oil collected in the 3-neck flask from the previous stage is once again tested for FFA using the same titration method explained earlier and the FFA is calculated to be 3%. On the basis of existing FFA 6.5 gm of NaOH is added to 150 ml of methanol in the separate beaker and mixed to prepare Methoxide mixture and the same is added to the oil present in the 3-neck flask. This mixture of oil and methoxide is agitated and heated at 60°C for 1hr30min. At the end of the process 2 distinct layers are obtained. The mixture is then transferred to conical shaped separating funnel and allowed to settle at atleast 2 to 3 hours as shown in the figure 5. Glycerine settles at the bottom and the biodiesel is
separated at the top. Glycerine is drained out from bottom and the biodiesel is taken for water wash.

Fig. 5: Separation of Glycerin

Table 1. The brief description of three stages

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameter</th>
<th>1st stage</th>
<th>2nd stage</th>
<th>3rd stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>150 ml</td>
<td>100 ml</td>
<td>125 ml</td>
</tr>
<tr>
<td>2</td>
<td>Orthophosphoric acid</td>
<td>3 ml</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>H2SO4</td>
<td>-</td>
<td>3 ml</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>KOH</td>
<td>-</td>
<td>-</td>
<td>6.5 gm</td>
</tr>
<tr>
<td>5</td>
<td>Reaction time</td>
<td>1hr30min</td>
<td>1hr30min</td>
<td>1hr30min</td>
</tr>
<tr>
<td>6</td>
<td>Settling time</td>
<td>1hr30min</td>
<td>1hr30min</td>
<td>1hr30min</td>
</tr>
<tr>
<td>7</td>
<td>Reaction temperature</td>
<td>55°C-60°C</td>
<td>50°C</td>
<td>60°C</td>
</tr>
</tbody>
</table>

5.3 Water wash

Water washing is done to remove any moisture and emulsion. To do this, water of about 30% by volume of the ester is added and heated the mixture to 1200°C for 1 hour to make the ester free from moisture. After heating, the mixture is once again transferred to the separating funnel where in again the water with any emulsion formed settled at the bottom. The upper layer is pure methyl ester i.e., bio-diesel, ready for the use in diesel engine. The biodiesel obtained is washed 3 times with water to remove the catalyst as shown in the figure 6 to get neat biodiesel which is free from moisture.

Fig. 6: Washing with hot water

Fig. 7: Sour Garcinia bio diesel

Fig. 8: Bio diesel and diesel blend.
VI. RESULTS AND CONCLUSIONS:

The properties of oil extracted from the seeds of Garcinia gummigutta listed in the Table 2 are similar to the properties of other vegetable oils listed in Table 3 which are widely used to produce biodiesel. Hence Garcinia gummigutta commonly known as Sour garcinia is considered as promising source for biodiesel.

Comparison of properties of conventional diesel and Sour Garcinia oil:

<table>
<thead>
<tr>
<th>SI.no</th>
<th>Property</th>
<th>For diesel</th>
<th>Sour Garcinia Oil</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Density in Kg/m3</td>
<td>850</td>
<td>915</td>
</tr>
<tr>
<td>2</td>
<td>Specific gravity</td>
<td>0.850</td>
<td>0.915</td>
</tr>
<tr>
<td>3</td>
<td>Kinematic viscosity in CST</td>
<td>2.83</td>
<td>27.00</td>
</tr>
<tr>
<td>4</td>
<td>Absolute Viscosity in poise</td>
<td>2.40</td>
<td>24.3</td>
</tr>
<tr>
<td>5</td>
<td>Flash point in 0C</td>
<td>76</td>
<td>163</td>
</tr>
<tr>
<td>6</td>
<td>Fire point in 0C</td>
<td>84</td>
<td>188</td>
</tr>
</tbody>
</table>

The FFA of raw oil of Garcinia gummigutta commonly known as Sour garcinia is 12% and the standard transesterification process is used to produce biodiesel from it and neat biodiesel is produced.

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