PRODUCTION OF SIMAROUBA OIL METHYL ESTER USING MIXED BASE CATALYST AND ITS CHARACTERISTICS STUDY

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ABSTRACT

Simarouba glauca is a rich source of fat, having a melting point of about 29°C and consisting of palmitic (12.81%), stearic (23.23%) and oleic (57.17%) as major fatty acids. It consists of about 36.04% of symmetrical monounsaturated-type triacylglycerols. Simarouba glauca oil is one of the tree borne oil which is available for biodiesel production in developing and underdeveloped countries. This paper deals with the transesterification of Simarouba glauca oil by means of methanol in presence of Sodium Hydroxide and Disodium Hydrogen ortho Phosphate as mixed base catalyst at less than 65°C. The viscosity of biodiesel is nearer to that of the diesel. The biodiesel is characterized by Gas Chromatography test and the important properties of biodiesel such as density, flash point, cloud point, pour point, carbon residue and ash content are found out and compared with that of diesel. The studies encourage the production of biodiesel from unrefined Simarouba glauca oil as viable alternative to the diesel fuel. The methyl ester content under these optimum conditions was 95%, and all the measured properties of Simarouba oil methyl ester (SOME) met the ASTM standards.

Keywords: Biodiesel, Mixed Base Catalyst, Simarouba Glaucu Oil, Transesterification, Gas Chromatography Test.

1. INTRODUCTION

Biofuels have become a matter of global importance because of the need for an alternative energy at a cheaper price and with less pollution[2]. Nowadays, most biodiesel is produced by the Transesterification of triglycerides of edible oils, non-edible oils, and waste vegetable oils using methanol with alkaline catalyst NaOH or NaOMe[12,13]. Homogeneous alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification[6]. A number of studies have been conducted on biodiesel processes, such as acid-catalyzed process[7,8], supercritical process[9,10], enzymatic process[11,12] and heterogeneous catalytic process. Due to noncorrosive, environmentally benign and easily separated from the liquid products the heterogeneous base catalysts can be designed to give higher activity, selectivity and longer catalyst lifetimes[13,14].

The heterogeneous catalytic process is expected to be an effective biodiesel production process with low cost and minimal environmental impact because of the possibility of simplifying the production and purification processes under mild conditions. Therefore, many heterogeneous catalysts for the transesterification of oils have been developed. The conversion in excess of 90% was achieved at a temperature of 100°C in the transesterification reaction of soybean oil with ETS-10 zeolite[18]. It has also been reported that the conversion to methyl ester reaches 87% with the potassium-loaded aluminacatalyst, when a mixture with a molar ratio of methanol to oil of 15:1 is refluxed for a reaction time 7
Besides these, there have been several other reports on heterogeneous catalysts for the transesterification of oils to biodiesel\cite{17-21}. Under roomtemperature, soybean oil and poultry fat can be converted to biodiesel using Nanocrystalline Calcium Oxides. The rate of reaction is slow and 6–24 hours is required to obtain high conversion with most active catalyst, and it is also observed that the deactivation of catalyst after eight cycles with soybean oil and after three cycles with poultry fat\cite{22}. A 93% conversion of *Jatropha curcas* oil is obtained using CaO as a catalyst, but the catalyst must be treated with ammonium carbonate solution and calcinated at high temperature\cite{23}. Tri Sodium phosphate (Na$_3$PO$_4$) is chosen as catalyst for biodiesel preparation from rapeseed oil. The transesterification is nearly completed within 20 minutes. The catalyst could be used repeatedly for 8 runs without any activation treatment and no obvious activity loss is observed.

In this work, we intend to examine amixed base catalyst in order to develop an effective biodiesel process catalyst with high activity and durability; hence the catalytic efficiency of mixed base (2% of Disodium hydrogen ortho phosphate and 0.1% of sodium hydroxide) in the transesterification reaction of Simarouba oil is evaluated with respect to the conversion of Simarouba oil to methyl esters. The effects of various reaction variables such as the molar ratio of methanol to oil (6:1), reaction temperature (65°C), mass ratio of catalyst to oil (2.1:1) and the reaction time (40 mins) on the conversion to methyl esters are investigated.

**Simarouba glauca** belongs to family simarubaceae, commonly known as “The Paradise Tree” or “King Oil Seed Tree”, is a versatile multipurpose evergreen tree having a height of 7-15 m with tap root system. It is mainly found in coastal hammocks throughout South Florida. In India, it is mainly observed in Andhra Pradesh, Karnataka and Tamil Nadu etc. It can adapt a wide range of temperature, has the potentiality to produce 2000-2500 kg seed/ha/year. The Simarouba fruit, shell and kernels shown in Fig 1.

### 1.1. Biodiesel Transesterification Reactions

Transesterification process consists of a sequence of three consecutive reversible reactions. i.e, conversion of triglycerides to diglycerides followed by diglycerides to monoglycerides. The glycerides were converted into glycerol and one ester molecule at each step. The methanolysis transesterification reactions\cite{12} are represented in Fig 2 & Fig 3.

If the oil contains more than 4% free fatty acids (FFA), then a two-step transesterification is applicable to convert the high FFA oils to its mono esters\cite{13}. In the first step, acid catalyzed esterification reduces the free fatty acid content of the oil. Alkaline transesterification process converts the products of the first step to its mono-esters and glycerol\cite{14} in the second step.

### 2. MATERIALS AND METHODS

#### 2.1. Materials

**2.1.1. Mixed base catalyst**

The homogeneous catalyst NaOH and the heterogeneous catalyst Na$_2$HPO$_4$ are mixed into the beaker and added into the solvent methanol. The mixed catalyst is a mixture of homogeneous and heterogeneous base catalyst. Hence the name mixed base catalyst.

**2.1.2. Simarouba oil**

The simarouba seeds are taken and oil is expelled using a mechanical expeller. It was noted that, 1kg of seeds produces 480ml to 500ml of oil. After the production the FFA of oil is tested and is used for biodiesel production.

**2.1.3. Methodology**

The oil is extracted from the kernel and biodiesel is produced. The obtained Simarouba Biodiesel is blended with Diesel and is used to run the engine. Performance study is carried out with different percentage of bio diesel blended with Diesel and the best combination is evaluated. The methodology is as shown in Fig 4.

### 3. EXPERIMENTAL METHODS

As the seeds crushed along with the shell, percentage of oil obtained will be 15% and without shell, oil obtained will be 25% to 35%. Hence the second method is preferred.

**3.1. Extraction of oil**

The extraction of oil from Simarouba seeds was done by using mechanical expeller and solvent extraction by soxhlet apparatus using methanol as solvent. The yields were given in Table 1.

**3.1.1. Soxhlet extraction**

To find out oil content of Simarouba seeds this method will be used. For 1000 gram of seeds, 480 ml simarouba oil is obtained. Hence the percentage of oil content is 48%.
3.1.2. Mechanical Expeller

The simarouba seeds are crushed to obtain kernel, these kernels will be used in mechanical expeller to get oil. The oil obtained was collected in a glass reagent container by filtering it with filters. The filtered oil left for 10-12hrs for settling of minute dust particles. After filter and settling, oil stored in a reagent glass bottles.

3.2. Determination of free fatty acid (FFA)

3.2.1: FFA calculation

\[
\text{FFA Content} = \frac{28.2 \times \text{Normality of NaOH} \times \text{Titration value}}{\text{weight of the oil}}
\]

\[
\text{FFA Content} = \frac{28.2 \times 0.1 \times 7.2}{10.2\text{gm}} = 1.99
\]

Note that the above formula contains 28.2 which is the molecular weight of oleic acid divided by ten. Oils are not made of only oleic acid hence this formula results in small errors, normally accepted.

3.2.2. Characterization of Simarouba oil

The fatty acid composition of the Simarouba oil was analyzed using gas chromatography(GC). The chromatograph consists of AGILENT 6890N equipped with flame ionization detector. Hydrogen was used as carrier gas at flow rate of 23ml/min. Column was packed with DB wax 30mm x 0.25mm. Injector port and detector port temperatures were maintained at 270°C and 280°C respectively. The data is given in Table 2.

Transesterification: 1ltr of Simarouba oil taken in a three neck flask with reflux condenser. Oil is heated up to 60°C and 250-500ml of methanol, 20gms of Disodium hydrogen ortho phosphate and 1gm of Sodium hydroxide catalyst was added. Process was made to run for about 60minutes as shown in Figure-5. Then, oil was transferred into separating funnel. Allowed to settle for about 7-8 hours. Three layers were formed as shown in figure-6. Upper layer is biodiesel, middle layer is glycerin and the lower layer is catalyst. Catalyst, glycerin and biodiesel were collected separately. The Yield after this process was found to be 92-95% of biodiesel, (920-950ml).

4. FUEL PROPERTIES

The following physiochemical properties listed of biodiesel produced were determined and compared with ASTM biodiesel standard values and diesel and the results are represented in Table-3.

5. RESULT AND DISCUSSION

5.1. Determination of physiochemical properties

5.1.1. Viscosity

Kinematic viscosity is the resistance offered by one layer of fluid over another layer. The viscosity is important in determining optimum handling storage, and operational conditions. Fuel must have suitable flow characteristics to ensure that an adequate supply reaches injectors at different operating temperatures. High viscosity can cause fuel flow problems and lead to stall out. The viscometer is shown in Figure 7. The kinematic Viscocity at 40°C is compared with SOME, Simarouba oil and Diesel, it is shown in Fig8.

Kinematic viscosity in Centistokes (Cst) =

\[
\text{(Number of seconds} \times \text{standard factor of the bulb viscometer used for testing)}
\]

5.1.2 Density

A hydrometer is the instrument used to measure the specific gravity (relative density) of biodiesel. That is the ratio of the density of water. The hydrometer is made of glass and consists of a cylindrical stem and bulb weighed with mercury or lead shot to make it float upright. The hydrometer contains a paper scale inside the stem, so that the specific gravity can be read directly. The hydrometer and measuring jar is shown in Figure 9. The Compared value of density is shown in Fig 10.

5.1.3. Flash point

The lowest temperature at which the vapor of a combustible liquid can be made to ignite momentarily in air is identified as the flash point and correlates to ignitibility of fuel. Low flash point can indicate residual methanol remaining from the conversion process. The flash point is often used as a descriptive characteristic of liquid fuel and it is
also used to characterize the fire hazards of liquids. “Flash point” refers to both flammable liquids and combustible liquids. The Pensky Martin flash point instrument is shown in Figure 11. The compared value of flash point is shown in Fig 12.

5.1.4. Oil properties

The fatty acid composition of mixed oil has been reported in Table 1. A total of 98.4% of fatty acids were identified in mixed Oil. It comprises of 36.04% Saturated fatty acids and 62.36% Unsaturated fatty acids. The maximum composition is Oleic acid (57.17%), which is an unsaturated fatty acid.

6. FIGURES & TABLES

![Fig 1: Simarouba dried fruits, broken fruits, shells and kernels (top to bottom)](image)

![Step I](image)

**Step I**

\[
\begin{align*}
\text{CH}_2\text{OOC-R}_1 \\
\text{CH-OOC-R}_2 + \text{CH}_3\text{OH} \rightarrow \text{HO-CH}_2 + \text{R}_2\text{COO-CH}_2 \\
\text{CH}_2\text{OOC-R}_3 \\
\end{align*}
\]

![Step II](image)

**Step II**

\[
\begin{align*}
\text{CH}_2\text{OH} \\
\text{CH-OOC-R}_2 + \text{CH}_3\text{OH} \rightarrow \text{HO-CH} + \text{R}_2\text{COO-CH}_3 \\
\text{CH}_2\text{OOC-R}_3 \\
\end{align*}
\]

![Step III](image)

**Step III**

\[
\begin{align*}
\text{CH}_2\text{OH} \\
\text{CH-OH} + \text{CH}_3\text{OH} \rightarrow \text{HO-CH}_2 + \text{R}_1\text{COO-CH}_3 \\
\text{CH}_2\text{OOC-R}_3 \\
\end{align*}
\]

![Glycerol & Esters](image)

**Fig 2: Transesterification Reaction of Triglycerides**
Fig 3: Mechanism of Transesterification Reaction

Fig 4: Methodology of Simarouba biodiesel production
Fig 5: Transesterification setup

Fig 6: Settling in separating funnel

Fig 7: Photograph of Kinematic bath instrument with cannon fenske tube
Fig 8: Comparison of Kinematic Viscocity (@40°C) of simarouba oil, SOME and Diesel

Fig 9: Hydrometer & Measuring jar with viscosity hydrometer immersed in it

Fig 10: Comparison of Density of simarouba oil, SOME and Diesel
Fig 11: Photograph of Pensky Martin Flash point instrument

Fig 12: Comparison of Flash point of simarouba oil, SOME and Diesel

**Tables:**

**Table 1: Percentage yield of oil from Simarouba Kernel**

<table>
<thead>
<tr>
<th>Extraction Method</th>
<th>Kernel condition</th>
<th>Yield in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical Expeller</td>
<td>Crushed</td>
<td>25-35</td>
</tr>
<tr>
<td>Soxhlet Apparatus</td>
<td>Powdered</td>
<td>55 –65</td>
</tr>
</tbody>
</table>

**Table 2: Chemical composition of Simaroubla Glaucia oil**

<table>
<thead>
<tr>
<th>Component</th>
<th>Carbons</th>
<th>Fatty acid%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>16:0</td>
<td>12.81</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>18:0</td>
<td>23.23</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>18:1</td>
<td>57.17</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>18:2</td>
<td>4.01</td>
</tr>
<tr>
<td>Arachidonic acid</td>
<td>20:4</td>
<td>1.18</td>
</tr>
</tbody>
</table>
Table 3: Shows various properties SOME, Standard Bio-diesel and Diesel

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>SOME</th>
<th>ASTM Standard Biodiesel</th>
<th>Diesel</th>
<th>Protocol (ASTM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity at 40°C (mm²/s)</td>
<td>4.7</td>
<td>1.9 to 6.0</td>
<td>2.54</td>
<td>D445</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.865</td>
<td>0.87 to 0.90</td>
<td>0.82</td>
<td>D4052</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>160</td>
<td>130 to 170</td>
<td>54</td>
<td>D93</td>
</tr>
<tr>
<td>Calorific value (kJ/kg)</td>
<td>37933</td>
<td>---</td>
<td>43500</td>
<td>D240</td>
</tr>
<tr>
<td>Ash, % w/w</td>
<td>Nil</td>
<td>0.02 max.</td>
<td>D482</td>
<td></td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>25</td>
<td></td>
<td>D2500</td>
<td></td>
</tr>
<tr>
<td>Carbon residue</td>
<td>Nil</td>
<td>0.05 max.</td>
<td>D524</td>
<td></td>
</tr>
</tbody>
</table>

6. CONCLUSIONS

Biodiesel has become more alternative recently because of its environmental benefits and the fact that it is made from renewable resources. Viscosity of the simarouba biodiesel was found low compared to the Simarouba oil and more compared to Diesel. The advantage of this method is catalyst can be reused for next process. Under optimal conditions, simarouba oil methyl esters yield of 92-95%, was achieved. All the properties are in the range of ASTM biodiesel standards and this can be promising factor to use Simarouba seeds as one of the biodiesel source.

7. REFERENCE

[15]. T. Jeyarani and S. Yella Reddy, “Cocoa Butter Extender from Simarouba glauca Fat”, [Received June 9, 2000; accepted November 23, 2000].


