Preparation of Biodiesel from Castor Oil by Two-Step Method

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Abstract

Current study reveals the production of biodiesel from non-edible oil such as castor oil (Ricinus Communis). Castor seed was collected from the local area of Sylhet region. Oil was extracted from seed by two different methods, Soxhlet extraction method and mechanical press method. Various properties of the raw oil were measured by standard methods. In the current study biodiesel was prepared from castor oil by two-step method due to higher Free Fatty Acid (FFA) content of raw oil. In two-step methods, the first step is acid catalyzed esterification followed by base catalyzed transesterification. The reaction parameters for esterification and transesterification were optimized. Finally, various properties of produced biodiesel from castor oil, such as specific gravity, viscosity, FFA, cloud point, flash point, saponification value, etc. were measured and compared with standard diesel and biodiesel properties.

Keywords: Castor oil; Two-step method; Free Fatty Acid; Esterification; Transesterification; Biodiesel.

1. Introduction

The fast growing population, rapid modernization and industrialization have relentlessly increasing the demand of energy in developing countries like Bangladesh. The current demand of energy in Bangladesh is mostly met from non-renewable resources such as natural gas and coal [1]. Since these sources are non-renewable in nature, the reserve will be depleted one day. In addition, the dependency on these fossil fuels, which are largely been imported, has serious implications on economy and environment. For this reason scientist are focus their view on the alternative renewable energy resource such as solar energy, biogas, biodiesel, wind power, tidal energy etc.

Biodiesel is a non-toxic, biodegradable, renewable fuel that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats [2]. Biodiesel has significantly lower emission than petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect [3].

In USA soybean oil is used for the biodiesel production because they have very high potentiality of producing soybean. But in our country the potentiality of edible oil sources is below the annual demand [4]. So the idea of biodiesel production from edible oil was omitted at the very beginning. And the concentrating field is now the forest oil seed production which is a potential source for Bangladesh. It was also investigated and found that non-edible oil can be used for biodiesel production because the price of non-edible oil is not too high and it will not contribute in high food price of the world market. Among these forest seeds like Castor, Nageswar, Rata, Palm, Chaulmoogra, Bakul, Kusum have sufficient oil content [5] and it does not require any additional land for plantation because they are available in our country.

Biodiesel is produced through a chemical reaction known as Transesterification. In Transesterification vegetable oil or animal fat (Triglyceride) react in presence of a catalyst with a primary alcohol to give the corresponding alkyl esters of the fatty acid mixture that is found in the parent vegetable oil or animal fat [6]. The amount of free fatty acid (FFA) in triglyceride plays a very important role in biodiesel production. Base catalyzed
trans-esterification reaction is widely used for biodiesel production from vegetable oil due to its faster kinetics than that of acid catalyzed process. But if FFA content in the oil is more than 2 wt%, the base catalyzed process is not feasible. FFAs act as a potential contaminant. They react with alkali catalyst to form soap. Soap can cause glycerol separation problem. The production of biodiesel from high FFAs containing feedstock needs a pretreatment to convert the FFAs to ester [7]. This pretreatment process is known as esterification. So, the production of biodiesel from low-quality feedstock consists of two steps: esterification and transesterification. This two steps approach is also known as acid catalysis followed by alkali catalysis.

In this paper, biodiesel production from castor oil was studied by two-step method since the FFA content of the raw castor oil was higher. In the first step (Esterification) sulfuric acid was used as catalyst and in the second step (Transesterification) sodium hydroxide was used as catalyst. Various reaction parameters for esterification and transesterification such as molar ratio of oil to methanol, catalyst concentration, reaction temperature and reaction time were optimized. Finally various properties of the produced biodiesel was measured and compared with the biodiesel standard and petro-diesel.

2. Materials and Methods

A. Chemicals

Methanol (99-100%), ethanol (99-100%), sodium hydroxide pellets (96%), potassium hydroxide pellets (>84%), phenolphthalein (pH 8.2 - 9.8), starch, acetone (99%), n-Hexane(96%), hydrochloric acid (37%), iso-propanol, iodine, sodium iodide, carbon tetrachloride etc. were purchased from Merck, Germany Ltd. All the chemicals used were analytical reagent grade.

B. Extraction of oil

Castor seeds were collected from road side of Sylhet region. Oil from the seed was extracted by mechanical press and soxhlet extraction method. Mechanical press is vertical, manual operated, cylindrical (4.3 cm ID) which have a spiral screw that convey the mass from the hopper to pressure raising area. Slow and continuous rotation of the mechanical press allows raising sufficient pressure for the extraction of oil. Here the spiral screw is used for random mixing, size distribution and passing the mass from hopper to pressure raising area. Oil drainage nozzles are located at the face of the expeller. Pressure raising area is located at the face of the expeller. In this expeller, pressure rises in slow and continuous rotation. The faster rotation of the expeller causes the back flow of the solid seed meal and it results the lowering of pressure. The input of seed grain should be controlled to prevent the loss of the seed because if the amount of raw seed is high, the extra seed meal stays within the screw and it is unable to reach in the pressure raising area. The back flow of seed grain should be adjusted with the rotation of the spiral screw. After oil extraction it was filtered. A Soxhlet Extraction unit was also used for oil extraction, where hexane was refluxed for 6 h for a given amount of kernel mass. The oil content of castor seed was found as 52.9% (wt/wt) and 45.6% (wt/wt) by soxhlet extraction method and mechanical press method respectively. The oil was stored at room temperature and used for further study.

C. Preparation of biodiesel from castor oil

In the current study biodiesel was prepared from castor oil by two step method. A two-step method, acid catalyzed esterification followed by base catalyzed transesterification, of higher FFA containing oil (castor oil) was adopted for the complete conversion of FFA and TG to fatty acid methyl esters [8]. The first step (esterification) was carried out at 60 °C and atmospheric pressure. The molar ratio of methanol/oil was 6/1. Typically, 100 ml oil was taken in a three-necked 500 mL round bottomed flask equipped with a reflux condenser. The flask was placed on an electric heater with a temperature controller and magnetic stirrer. Sulfuric acid (2 wt% of oil) was mixed with required amount of methanol and transferred into the reaction medium. The reaction continued until the FFA of oil reduces below 2 wt%. After that, the reaction contents were cooled to room temperature and reaction product was washed with hot water until clear water found. The organic phase was collected and dried under vacuum at 100 °C for 30 min. This product was then subjected to transesterification reaction.

Transesterification reaction was conducted by the method described by Sadyut et. al. [9]. For transesterification reaction sodium methoxide solution was prepared by dissolving sodium hydroxide pellets (1 wt% of oil) in required amount of methanol. Molar ratio of methanol to oil was taken 6:1 for the total conversion of TG to biodiesel. The trans-esterification reaction was performed in a flask under vigorous stirring at 60°C. After a certain period reaction was stopped by adding stoichiometric amount of HCl. After the reaction period, the reaction product was allowed to stand 12-14 hour in a separatory funnel. Two separate layers were observed. Upper layer was methyl ester (Biodiesel) and lower layer were a mixture of soap, crude glycerin, residual methanol and lye catalyst. The
Biodiesel layer was separated and this layer was opaque as it contained some catalyst, methanol, triglyceride and soap. For purification of the biodiesel, washing with hot water until clear water found. The washed biodiesel was then dried at 80-100 °C under vacuum in rotary evaporator. The effect of different reaction parameters such as methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time were observed and optimized.

D. Analytical methods for oil and biodiesel

FFA in the oil and biodiesel samples was analyzed by the method described in AOCS Aa 6-38 [10]. To determine FFA of sample, 4–5 gm of samples were dispersed in isopropanol (75 mL) and hexane (15 mL) followed by titration against 0.25 N NaOH solution. Saponification value (SV) was determined by standard method described by Jeffery et.al. [11]. Typically, 1 gm sample was taken with 25 mL alcoholic KOH solution, heated for 1 hr in a steam bath with occasional shaking and titrated the excess KOH with the 0.5 M hydrochloric acid solution. The iodine value (IV) was determined by the method describe in American Oil Chemist’s Society. To determine IV, titrating the mixture of tested fuel and chemical reagents against 0.01 N sodium thiosulfate solution until the disappearance of the blue color. IV was calculated by the following Eq. 1:

\[
\text{Iodine value} = \frac{(B-S) \times N \times 0.001269}{W}
\]

Where, S and B are the amounts (in unit of mL) of sodium thiosulfate solution required for titration of the tested sample and blank sample respectively. N is the molar concentration (in unit of mol/L) of sodium thiosulfate solution and W is the weight (in unit of gm) of the tested sample.

Physical properties such as moisture content, specific gravity and calorific value of the oil were determined by following ASTM D 1744 (Karl Fisher method), ASTM D 1480/81 and ASTM D 240 respectively. Viscosity, flash point, pour point and cloud point were determined by standards ASTM D 445, ASTM D 93 (Pensky–Martens Flashpoint Apparatus, Lazer Scientific Inc., Germany), ASTM D 2500 and ASTM D 97 respectively.

3. Result and Discussion

A. Characterization of castor oil

Various physical properties of raw castor oil were measured using standard methods and are represented in table 1.

<table>
<thead>
<tr>
<th>Property name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>Specific gravity at 25°C</td>
<td>0.95</td>
</tr>
<tr>
<td>FFA content (wt %)</td>
<td>13.6</td>
</tr>
<tr>
<td>Viscosity (mm²/sec)</td>
<td>352</td>
</tr>
<tr>
<td>Saponification value (mg KOH/gm Oil)</td>
<td>232.1</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>876.92</td>
</tr>
</tbody>
</table>

*Molecular weight was determined from the composition of the castor oil [12].

B. Preparation of biodiesel from castor oil

Biodiesel was prepared from castor oil by two-step method. In the first step (esterification) FFA reduces below 2% within 1 hour but viscosity reduces to 81.3 mm²/sec from 352 mm²/sec. In the second step (transesterification) viscosity reduces to 11.6 mm²/sec within 30 min and a slight reduction in FFA occurs. Four reaction parameters that affect the esterification and transesterification reaction are oil to methanol molar ratio, catalyst concentration, reaction temperature and time. All the reaction parameters were optimized and the results are discussed below.

B. I. Effect of oil to methanol molar ratio

The methanol to oil molar ratio is one of the important factors that affect the conversion of esterification and transesterification reaction. Since both reactions are reversible, the excess amount of alcohol is used in order to shift the reaction equilibrium, to avoid the reverse reactions and to accelerate the process [13]. Reactions were carried out at different oil to methanol molar ratios at a temperature of 60°C. Reaction time was 1hr for esterification and 30
min for transesterification. Catalyst concentration was 5wt% of oil (H₂SO₄) in esterification reaction and 1wt% of oil (NaOH) for transesterification reaction. The results are represented in figure 1 and figure 2.

From figure 1 it was found that the reduction of FFA occurs with the increase in oil to methanol molar ratio. FFA reduces below 2 wt% within 1 hr at oil to methanol molar ratio of 1:6 which is considered as optimum oil to methanol molar ratio for esterification reaction. Similarly, from figure 2 it was observed that the viscosity decreases as the molar ratio of oil to methanol increases. At 1:6 molar ratio of oil to methanol the viscosity reduces to 11.6 mm²/s. Further increase in molar ratio of oil to methanol, viscosity remain constant. So, optimum molar ratio of oil to methanol was also found as 1:6.

B.II. Effect of catalyst concentration
Catalyst enhances the rate of a reaction. With a higher concentration of catalyst it requires less time to reach the reaction in completion. Esterification and transesterification reaction were carried out at different catalyst
concentrations and the results are represented in the figure 3 and figure 4. Sulfuric acid was used as catalyst for esterification and NaOH for transesterification. Both reactions were carried out at oil to methanol molar ratio of 1:6 and temperature was 60°C. Reaction time was 1 hr for esterification and 30 min for trans-esterification.

![Graph showing the effect of catalyst concentration on esterification reaction.](image1)

**FIG. 3.** Effect of catalyst concentration on esterification reaction [molar ratio of oil to methanol = 1:6, reaction time = 1 hr, Temperature = 60°C, under reflux with vigorous stirring].

![Graph showing the effect of catalyst concentration on transesterification reaction.](image2)

**FIG. 4.** Effect of catalyst concentration on transesterification reaction [molar ratio of oil to methanol = 1:6, reaction time = 30 min, Temperature = 60°C, under reflux with vigorous stirring].

From figure 3 it was observed that rate of the reaction increases as the concentration of catalyst increased. Only 1 wt% of catalyst (H₂SO₄) was sufficient for the reduction of FFA below 2 wt% within 1 hour. Further increase in catalyst concentration, FFA did not reduce significantly. So, the optimum catalyst concentration was 1 wt% of oil for esterification. But from figure 4 it was found that the viscosity increases as the concentration of catalyst increased. This is because the more concentration of catalyst the more tendency of soap formation which converts to FFA during catalyst neutralization. Higher percentage of FFA enhances the final viscosity of the biodiesel. The minimum
concentration of catalyst that requires for the completion of reaction was 0.5 wt% of oil which was the optimum concentration of catalyst for transesterification.

**B. III. Effect of Temperature**

Temperature is an important parameter that affects the esterification and transesterification reaction. There is an increase in the rate of reaction with the increase in temperature. The reaction was carried out at different temperatures with optimum methanol molar ratio and catalyst concentration. Reaction time was 1 hr for esterification and 30 min for trans-esterification. The results are presented in figure 5 and figure 6.

![Graph](attachment:image1)

**FIG. 5.** Effect of temperature on esterification reaction [molar ratio of oil to methanol = 1:6, catalyst (H$_2$SO$_4$) concentration = 1wt% of oil, reaction time = 1 hr, under reflux with vigorous stirring].

![Graph](attachment:image2)

**FIG. 6.** Effect of temperature on transesterification reaction [molar ratio of oil to methanol = 1:6, catalyst (NaOH) concentration = 0.5wt% of oil, reaction time = 1 hr, under reflux with vigorous stirring].
From figure 5 and figure 6 it was found that better results were obtained as the temperature increased. For esterification reaction 50°C was the optimum temperature and for transesterification reaction it was 60°C.

**B. IV. Optimum reaction time**

Optimum reaction time for esterification and transesterification was observed. The results are represented in figure 7 and figure 8. For esterification the optimum time was 60 min and for transesterification it was 30 min.

**FIG. 7.** Effect of time on esterification reaction [molar ratio of oil to methanol = 1:6, catalyst (H₂SO₄) concentration = 1wt% of oil, Temperature = 60°C, under reflux with vigorous stirring].

**FIG. 8.** Effect of time on transesterification reaction [molar ratio of oil to methanol = 1:6, catalyst (NaOH) concentration = 0.5wt% of oil, Temperature = 60°C, under reflux with vigorous stirring].
Optimum parameters for esterification and transesterification reactions are given in Table 2.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Oil: methanol</th>
<th>Catalyst concentration</th>
<th>Temperature</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esterification</td>
<td>1:6</td>
<td>1 wt% of oil</td>
<td>50°C</td>
<td>60 min</td>
</tr>
<tr>
<td>Transesterification</td>
<td>1:6</td>
<td>0.5 wt% of oil</td>
<td>60°C</td>
<td>30 min</td>
</tr>
</tbody>
</table>

### C. Characterization of biodiesel

Various properties of produced biodiesel was measured using standard methods and compared with soybean oil methyl ester and diesel standard. The results are given in Table 3. The viscosity and specific gravity of the produced biodiesel was higher than biodiesel standard. This biodiesel was blended with diesel with different volumetric proportion. The results are presented in Figure 9. From the figure it can be seen that the mixture of 70% biodiesel and 30% diesel by volume named B70 match with the physical properties of biodiesel standard. The properties of B70 are also given in Table 3.

![Fig. 9: Blending curve of biodiesel with petro-diesel.](image)

### Table 3: Comparison of properties of biodiesel produced from castor oil with soybean oil biodiesel and diesel standard.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Color</td>
<td>Pale yellow</td>
<td>Pale yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity at 25°C</td>
<td>0.9</td>
<td>0.88</td>
<td>0.885</td>
<td>0.835</td>
</tr>
<tr>
<td>Viscosity mm²/s at 23°C</td>
<td>11.6</td>
<td>6.3</td>
<td>4.08 at 40°C</td>
<td>3.8 at 40°C</td>
</tr>
<tr>
<td>FFA Weight%</td>
<td>1.1</td>
<td>1.8</td>
<td>Trace</td>
<td>-</td>
</tr>
<tr>
<td>Saponification value (mg of KOH/gm of oil)</td>
<td>212</td>
<td>210.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iodine value</td>
<td>71.8</td>
<td>70.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cetane Index</td>
<td>55.9</td>
<td>56.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calorific Value (Mj/Kg)</td>
<td>To be measured</td>
<td>To be measured</td>
<td>39.76</td>
<td>42.25</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>183</td>
<td>168</td>
<td>169</td>
<td>145</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>3</td>
<td>3</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>6</td>
<td>6</td>
<td>-3</td>
<td>-16</td>
</tr>
</tbody>
</table>
4. Conclusion

Biodiesel was prepared from non-edible higher FFA containing castor oil by two-step method. Various reaction parameters for both steps (esterification and transesterification) were optimized. The viscosity of the oil was reduced from 253 mm²/s to 11.6 mm²/s and the FFA content was reduced from 13.6 wt% to 1.1 wt%. Viscosity was slightly higher than the biodiesel standard. The produced biodiesel from castor oil can be used in diesel engine by blending with petro-diesel. B70 was a mixture of 70% by volume of produced biodiesel and 30% by volume of petro-diesel. The viscosity of B70 is similar with biodiesel standard. This product can be successfully used as diesel in diesel engine.

5. References