Production and Characterization of Biodiesel from Cottonseed oil

Anil R. Shet, Shashank S. Kouloorkar, Deepa M. Moolya, Rajath S. Poovjari, Jagadish V. Reddy
Department of Biotechnology, B.V. Bhoomaraddi College of Engineering and Technology, Hubli, Karnataka 580031, India.
Corresponding author email: shet_anil@rediffmail.com

ABSTRACT
Reserves shortage and price increase are causing a growing substitution of fossil fuels with fuels derived from vegetable origin such as ethanol or biodiesel. Biodiesel, the most promising alternative diesel fuel, has received considerable attention in recent years due to its following merits: biodegradable, renewable, non-toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal diesel. In this research, the variables affecting the ester yield and characteristics of the biodiesel produced from cottonseed oil were studied. The highest biodiesel yield of 92% was obtained under the conditions of 1:1 methanol to oil molar ratio, 0.75% NaOH catalyst and 150 minutes reaction time. The properties like viscosity, flash point, carbon residue and specific gravity of produced biodiesel were investigated and found to be within the ASTM standards of biodiesel.

Keywords: Cottonseed oil, Biodiesel, Transesterification, Characterization, Free fatty acid.

INTRODUCTION
Biodiesel, the most promising alternative diesel fuel, has received considerable attention in recent years due to its following merits: biodegradable, renewable, non-toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal diesel. In addition, it meets the currently increasing demands of world energy that, in a large degree, is dependent on petroleum based fuel resources, which will be depleted in the foreseeable future if the present pattern of energy consumption continues [1]. Biodiesel is derived from vegetable oils or animal fats through transesterification. Transesterification is also called alcoholysis, which uses alcohols in the presence of catalyst that chemically breaks the molecules of triglycerides into alkyl esters as biodiesel fuels and glycerol as a by-product. The commonly used alcohols for the transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are adopted most frequently, particularly the former due to its low cost [2]. The three basic methods of ester production from oil/fat are the base-catalyzed transesterification, the acid catalyzed transesterification and enzymatic catalysis. Alkali catalyzed transesterification process is the common process for production, because it can achieve high purity and high yield of biodiesel in short time. Transesterification reactions have been studied for many vegetable oils such as soybean [3], rapeseed [4], sunflower [5], safflower [6], canola [2], palm [7] and fish oil [8]. In recent years, there exist active researches on biodiesel production from cottonseed oil, of which the conversion between 72% and 94% was obtained by enzyme catalyzed transesterification when the refined cottonseed oil reacted with short-chain primary and secondary alcohols. The application of solid acid catalysts on cottonseed oil transesterification was investigated. The results showed that the yield of methyl ester was above 90% after 8 hours of reaction. In contrast, transesterifying cottonseed oil by microwave irradiation could produce a biodiesel yield in the range of 89.5-92.7% [1]. No matter what kind of catalysts or approaches were applied, all those studies aimed to produce high yield of biodiesel by optimized reaction conditions based on optimized parameters in terms of alcohol/oil molar ratio, catalyst concentration, reaction temperature, and reaction time. However, nearly in all studied cases, there existed complex interactions among the variables that remarkably affected the biodiesel yield. The determination of biodiesel fuel quality is an issue of great importance to the successful commercialization of this fuel [1]. Although cottonseed oil was the first commercial cooking oil in the U.S, it has progressively lost its market share to some vegetable oils that have larger production and less cost. However, regarding the active researches on biodiesel production from vegetable oils, there is a promising prospective for the cottonseed oil as a feedstock for biodiesel production, which may enhance the viability of the cottonseed industry. The focus of this research was to study the effect of various parameters on biodiesel production from cotton seed oil and characterization of the produced biodiesel.
MATERIALS AND METHODS

Raw materials and chemicals
Cotton seed oil was brought from local market, Hubli, Karnataka State, India. Methanol, Sodium hydroxide and Bromocresol-Green indicator used in this research, were obtained from Sd fine chemicals pvt limited, India.

Free Fatty Acid (FFA) content
In order to determine the percent of free fatty acid in the oil, the following method was used. The oil was first mixed with methanol to which 0.1% Sodium Hydroxide was added till all of the FFA has been reacted. This was confirmed by checking the pH of the mixture. A pH of about 9 signifies all of the FFA has been reacted. The 0.1% NaOH was prepared by adding 1 gram of NaOH to 1000ml distilled water. 10ml of Methanol was taken in a 50ml conical flask to which 1ml of oil was added and mixed properly. Bromocresol-Green indicator was added to the solution and titrated it against 0.1% NaOH. The solution was mixed properly using a swirling action between the additions of NaOH until a blue-green color was obtained [9].

Transesterification Process
In the transesterification of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. To make it possible, a catalyst is added to the reaction.

\[
\begin{align*}
\text{CH}_2\text{OOC-R}_1 + \text{CH-OOC-R}_2 + 3\text{R'}\text{OH} & \rightleftharpoons \text{R}_1\text{COO-R'} + \text{CH}_2\text{OH} + \text{CH}_2\text{OOC-R}_3 \\
\text{Glycerides} & \text{ Alcohol} & \text{Esters} & \text{Glycerin}
\end{align*}
\]

Fig. 1. Chemical reaction for biodiesel production

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride, monoglyceride is produced and in the last step, from monoglycerides glycerine is obtained. In all these reactions esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product [9].

\[
\begin{align*}
\text{Triglycerides (TG)} + \text{ROH} & \rightleftharpoons \text{Diglycerides (DG)} + \text{R'}\text{COOR}_1, \\
\text{Diglycerides (DG)} + \text{ROH} & \rightleftharpoons \text{Monoglycerides (MG)} + \text{R'}\text{COOR}_2, \\
\text{Monoglycerides (MG)} + \text{ROH} & \rightleftharpoons \text{Glycerin (GL)} + \text{R'}\text{COOR}_3.
\end{align*}
\]

Fig. 2. Steps involved in the transesterification process.

Biodiesel production
Biodiesel production from cottonseed oil was carried out for different parameters like catalyst type (NaOH and KOH), catalyst concentration (0.25%, 0.75% and 1.25%), Reaction time (0.5h, 1.5h and 2.5h) and Alcohol to oil ratio (1:1, 2:1 and 8:1).
Appropriate volume of methanol was measured and poured into a 250 ml conical flask as per the required ratio. The NaOH catalyst was weighed and mixed with methanol for about 15 to 20 minutes until all catalyst is dissolved. The flask was covered with aluminum foil during shaking to reduce the loss of alcohol by evaporation. The oil was pre-heated at temperature of 45ºC in water bath to melt coagulated oil molecules. 25 ml of heated oil was measured and poured into the conical flask, which already contained alcoxide mixture. This oil and alcoxide mixture was kept in shaker at 200 rpm and room temperature. After taking out from shaker, the product of the reaction was exposed to open air so that excess methanol gets evaporated. And then this mixture was allowed to settle using separating funnel for overnight. Crude ester was present at the top and glycerol at the bottom. Glycerol was removed and the biodiesel which was remaining in the separating funnel was collected and washed with water. Water and biodiesel was shaken gently for 1-2 minutes and then allowed to settle. It was washed several times until the washed water became clear. At the end, biodiesel was heated to remove any moisture content present after washing with water. For different parameters, the amount of ester produced was measured and the percentage of biodiesel yield was calculated by \([\frac{\text{Volume of BD produced}}{\text{Volume of oil used}}] \times 100\) [10].

**Biodiesel characterization**

**Determination of Specific gravity**
A clean and dry bottle of 25ml capacity was weighed \((W_0)\) and then filled with the biodiesel sample, stopper inserted and reweighed to give \((W_1)\). The sample was substituted with water after washing and drying the bottle and weighed to give \((W_2)\). The specific gravity was determined by \(\frac{W_1-W_0}{W_2-W_0}\) [11].

**Determination of viscosity**
Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. 15ml of water was sucked through suction pipe till it crossed the upper mark of the viscometer, and then the time required by the water to flow from upper-mark to lower-mark was noted down with the help of a stopwatch. Further 15ml of biodiesel sample was taken in a viscometer. It was sucked through suction pipe till the sample crossed the upper mark of the viscometer. Then, the time required by the sample to flow from upper-mark to lower-mark was noted. Relative Viscosity was determined by the equation \(\frac{T_o}{T_w}\), Where \(T_o = \text{Time taken for biodiesel to travel from upper mark to lower mark}\) and \(T_w = \text{Time taken for water to travel from upper mark to lower mark}\).

**Determination of Flash Point**
Flash point was measured using Pensky Marten’s apparatus. The cup was rinsed, cleaned and dried before starting the test. The cup was filled up to the mark with the biodiesel sample and covered with the lid. Thermometer was inserted such that, the bulb got immersed in the sample and care was taken that stirrer would not touch the thermometer. The initial temperature of the sample was noted down. Heater was started and the power level was set such that temperature of sample rises at the rate of 3ºC/min. The stirrer rotated at 2 rev/sec. Test flame was applied by operating shooter. For every 2ºC rise in temperature, the test flame was brought near cup surface for observing the phenomenon. When flash appeared on the surface of cup, the temperature was noted down and taken as Flash point.
Determination of Carbon Residue
Empty weight of the crucible was taken using a weighing balance. Then, 5ml of biodiesel sample was poured in a crucible and was weighed again. This crucible was placed in a skid more iron crucible and lid was placed over it. The lid of the skid more crucible contained tube type opening for the escape of volatile matter. The combination was then placed in a wrought iron crucible and lid was placed. The above combination was covered by a chimney shaped iron hood. The wrought iron- crucible was heated slowly for 10 minutes till the flame appeared. Slow heating was continued for 5 more minutes and finally, strong heating for about 15 minutes till the vapors of all volatile material was burnt completely. The apparatus was then allowed to cool and weight of the residue left was determined. Carbon residue was calculated by \( C = W_1 - W_2 \), where \( W_1 \) = Empty weight of the crucible, \( W_2 \) = Weight of crucible with carbon residue [11].

Results and Discussion

Determination of % FFA content
Higher amount of free fatty acids (>1% w/w) in the feedstock can directly react with the alkaline catalyst to form soaps, which are subject to form stable emulsions and thus prevent separation of the biodiesel from the glycerol fraction and decrease the yield, it is better to select reactant oils with low FFA content or to remove FFA from the oil to an acceptable level before the reaction [12]. The below table shows the %FFA of cottonseed oil to be equal to 0.357 % which is below 2.5%. So the %FFA content of the oil taken for the research is within the limits.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Titration reading in ml</th>
<th>Free Fatty Acid content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cottonseed Oil</td>
<td>0.5</td>
<td>0.357</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Titration value in ml</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>% FFA content</td>
<td>0</td>
<td>0.357</td>
<td>0.715</td>
<td>1.073</td>
<td>1.431</td>
<td>1.789</td>
<td>2.146</td>
<td>2.504</td>
<td>2.862</td>
</tr>
</tbody>
</table>

Effect of Catalyst Type
In this experiment, different catalyst types were used to study the effect on biodiesel production. The reactions were carried out using 0.75% catalyst concentration, 1:1 methanol to oil molar ratio, 150 minutes reaction time and room temperature. From the figure 4, it can be seen that NaOH catalyst gave the higher ester yield compared to KOH catalyst.

Effect of Catalyst Concentration
The effect of NaOH concentration on ester yield was studied in the range of 0.5 to 1.25% (weight of NaOH/ weight of oil). The reaction temperature and time were kept constant at 30°C and 150 minutes respectively. It was found that the biodiesel yield initially increased and then decreased as the amount of
catalyst increased from 0.5% to 1.25%. High concentration of NaOH reduced the yield because of high soap formation and lead to undesirable extra processing cost [13].

![Fig. 5. Effect of catalyst concentration on biodiesel yield.](image)

**Effect of alcohol to oil molar ratio**

Different methanol to oil molar ratios was used, 1:1, 2:1 and 8:1. The reactions were carried out using 0.75% sodium hydroxide for 150 minutes at room temperature. Figure 6 shows the yield of biodiesel from cottonseed oil by using different methanol to oil molar ratio. The results show that increasing methanol to oil molar ratio increased the yield of biodiesel production. Methanol to oil molar ratio of 1:1 gave the optimum yield of biodiesel among them. The high molar ratio of alcohol to oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps to drive the equilibrium to back left, lowering the yield of esters [14].

![Fig. 6. Effect of methanol to oil ratio on biodiesel yield.](image)

**Effect of Reaction Time**

In this experiment, reaction time was chosen between 30 minutes to 150 minutes. The reactions were carried out by using 1:1 methanol to oil molar ratio, 0.75% NaOH concentration and at room temperature. Figure 7 shows the yield percentage of biodiesel at different reaction times. From the results, 150 minutes of reaction time gave better yield when compared to 30 minutes. The longer the reaction time, the more the hydrolysis of ester would occur. It might produce many free fatty acids at the end, and these FFAs would involve in soap formation, thus reducing the biodiesel yield [10].
Biodiesel Characterization

The characterization of biodiesel was done by studying the different properties like viscosity, specific gravity, carbon residue and flash point. The experimental values obtained were tabulated and compared with those of ASTM values, which were found to be satisfactory.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM values</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (g/cc)</td>
<td>0.860-0.900</td>
<td>0.9716</td>
</tr>
<tr>
<td>Viscosity (mm²/s)</td>
<td>1.9 – 6.0</td>
<td>2.04</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>&gt; 130</td>
<td>170</td>
</tr>
<tr>
<td>Carbon residue (% mass)</td>
<td>0.050</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Conclusion

Several parameters affecting biodiesel production from Cottonseed oil were studied. The free fatty acid of the cottonseed oil was determined and found to be below 2.5%. The optimum values of different parameters affecting the biodiesel production were as follows: 0.75% NaOH (w/w_oil) concentration, 1:1 methanol to oil molar ratio and 150 minutes reaction time. The results showed that NaOH was the best catalyst for this reaction condition. It was found that excessive catalyst concentration results in formation of soap and cause emulsion formation during purification of biodiesel which results in decreased ester yield. Increasing the alcohol to oil molar ratio decreased the ester yield, because of the presence of glycerin in the solution. The experimental values of different properties were found to meet the international standards. Overall results showed that it was effective to produce good quality biodiesel from Cottonseed oil which could be used for diesel engine.
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References