

## **PREPARATION AND CHARACTERIZATION OF BIODIESEL FROM CASTOR OIL BY THREE-STEP METHOD**

**Kaniz Ferdous<sup>1\*</sup>, M. Rakib Uddin<sup>1</sup>, Anjan Deb<sup>1</sup>, Jannatul Ferdous<sup>1</sup>, Maksudur R. Khan<sup>1,2</sup>, M. A. Islam<sup>1</sup>**

<sup>1</sup>Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology (SUST), Sylhet 3114, Bangladesh.

<sup>2</sup>Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia

<sup>1\*</sup>Corresponding Author: Kaniz Ferdous, Ph.D student, Shahjalal University of Science and Technology, Sylhet.

Email: engr\_kaniz@yahoo.com; mruddincep@gmail.com; anjan\_cep@yahoo.com; rumkyj@yahoo.com; mrkhancep@yahoo.com; islamsust@yahoo.com.

**Abstract:** *In this paper, production of biodiesel from castor oil, containing 27.8% free fatty acid (FFA), was investigated. Raw oil was collected from castor seed by mechanical press method and soxhlett extraction methods. Various properties of the raw oil were measured by standard method. Since the acid value of the raw oil was higher, biodiesel cannot be produced from castor oil by base catalyzed transesterification reaction. A three-step method was studied for biodiesel production from castor oil. In the three-step method, the first step is saponification followed by acidification to produce FFA and finally esterification of FFA to produce biodiesel. Silica gel was used during esterification reaction to adsorb water produced in the reaction. Hence the reaction rate was increased. Second order kinetic model was proposed for esterification reaction and experimental data were fitted. Finally various properties of the biodiesel were measured and compared with the standard biodiesel and conventional diesel fuel.*

**Key words:** biodiesel, saponification, esterification, kinetics.

### **1. INTRODUCTION**

Since traditional fossil energy resources are limited and greenhouse gas emissions are becoming a greater concern, research is now being directed towards the use of alternative renewable fuel that are capable of fulfilling an increasing energy demand. One of the more promising approaches is the conversion of vegetable oils and other feed stocks, which primarily contain triglycerides and free fatty acids (FFA), into biodiesel. This is an attractive alternative (or extender) to petro diesel fuel due to well-known advantages [1]: (1) lower dependence on foreign crude oil, (2) renewable resources, (3) limitation on greenhouse gas emissions because of the closed CO<sub>2</sub> cycle, (4) lower combustion emission profile (especially SO<sub>x</sub>) [2], (5) potential improvement of rural economies, (6) biodegradability, (7) use without

engine modifications, (8) good engine performance, (9) improved combustion because of its oxygen content, (10) low toxicity and finally (11) ability to be blended in any proportion with regular petroleum-based diesel fuel.

Depending upon the climate and soil conditions, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. For example, soyabean oil in the US, rapeseed and sunflower oils in Europe, palm oil in South-east Asia (mainly Malaysia and Indonesia) and coconut oil in the Philippines are being considered [3]. Currently, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern

because they compete with food materials – the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long-term. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel. The use of non-edible oils when compared with edible oils is very significant in developing countries because of the tremendous demand for edible oils as food, and they are far too expensive to be used as fuel at present [4,5]. Recently the planning commission of India has recommended Karanja and Jatropha for biodiesel production in India [6].

The manufacturing process of biodiesel can be divided into three systems based on the type of catalyst used in the transesterification reaction, which are strong alkali, strong acid and enzyme. The process of transesterification by a strong alkali catalyst has a short reaction time. Only a small quantity of catalyst is required in the transesterification reaction and it is therefore, widely applied in the commercialized biodiesel production. In contrast, the process of transesterification by a strong acid catalyst requires a longer reaction time but it tolerates more water and FFA in the reactant mixture during the transesterification reaction and is therefore, suitable to be used in the pre-treatment of oil prior to carrying on with the strong alkali-catalyzed process. Moreover, the enzyme catalyst process has the disadvantages of both higher production cost and lower conversion rate, which prevents it from being applied to mass biodiesel production [7].

Due to higher FFA content and viscosity of raw castor oil, transesterification reaction cannot be used for biodiesel production. Three-step method can be used for biodiesel preparation from higher FFA containing oil [8].

The objectives of the present study was synthesised biodiesel from castor oil and the physical properties of the produced biodiesel were measured. Also the kinetics of esterification reaction was studied and a second order kinetic model was proposed and the experimental data were fitted to this model.

## 2. MATERIALS AND METHODS

### 2.1 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%), isopropanol, iodine, sodium iodide, glacial acetic acid, bromine, carbon tetrachloride etc. were purchased from Merck, Germany. All the chemicals used were analytical reagent grade.

### 2.2 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. A vertical, manual operated, cylindrical (4.3 cm ID) mechanical press was constructed which have a spiral screw that conveys the mass from the hopper to pressure raising area. Slow and continuous rotation of the press allows raising sufficient pressure for the extraction of oil. After oil extraction it was filtered. A Soxhlet Extraction unit was used for oil extraction, where hexane was refluxed for 6 h for a given amount of karnel mass. The oil content of castor seed was found 48.3% (v/w) by press method and 62.8% by soxhlet extraction method.

### 2.3 Preparation of biodiesel from castor oil

Transesterification process has been widely used to reduce high viscosity of the oil. Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous catalysts [1]. Although, alkali-catalyzed transesterification is much faster than acid catalyst, it is not suitable for castor oil transesterification because castor oil contains large amounts of FFA. Alkaline catalysts are very sensitive to FFA. FFA can react with an alkali catalyst to produce soap and water, which diminishes the ester yield [7,9-10]. Homogeneous acid catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction and hence is not popular for industrial production of biodiesel [11]. Castor oil that was used in this study contains 27.8% FFA. To remove this problem, biodiesel was prepared from castor oil by three-step method [8]. In three-step method castor oil was saponified, acidified and esterified sequentially. Saponification process was carried out in a 500 mL three-necked flask equipped with reflux condenser, magnetic stirrer and thermometer. 50 gm castor oil was reacted with different stoichiometric amount of sodium hydroxide at temperature of 100 °C under reflux with vigorous stirring for different time. The reaction was stopped by cooling the reaction mixture. The molar ratio of oil to sodium hydroxide and the reaction time was optimized. After saponification, the following second step was acidification in which the soap solutions were treated with different stoichiometric amount of concentrated hydrochloric acid at a temperature of 60-70 °C with vigorous stirring. After dissolving the soap, the FFA contents were separated in separatory funnel. The FFA content was determined by

titrimetric method. The molar ratio of soap to HCl was optimized.

In the final step, the FFA was converted to biodiesel by acid catalyzed esterification reaction with methanol. Reactions were carried out at 60<sup>0</sup> C and atmospheric pressure. Typically, 50 g FFA was put into a three-necked 250 mL round bottomed flask equipped with a reflux condenser and rubber septum. The flask was placed in an electric heater with a temperature controller and magnetic stirrer. Required amount of sulfuric acid was mixed with methanol and transferred into the reaction medium. Samples were withdrawn in every 5 min and FFA content was analyzed. After 120 min when the FFA content reduced to a constant level, the remaining contents were cooled to room temperature and reaction product was washed with hot water. The organic phase was collected and dried under vacuum at 100<sup>0</sup> C for 30 min. Effect of oil/methanol molar ratio, catalyst concentration and temperature was investigated. In esterification reaction water is produced, which decrease the reaction rate. In order to eliminate this problem silica gel was used in esterification reaction to adsorb the water produced in esterification reaction.

## 2.4 Analytical methods for oil and biodiesel

FFA in the oil and biodiesel samples was analyzed by the method described in AOCS Aa 6-38 [12]. To determine FFA of sample, 4–5 g 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 [13]. Typically, 1 g sample was taken with 25 mL alcoholic KOH solution, heated for 1 h 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 titrating with 0.01 N sodium thiosulfate solution to the mixture of tested fuel and chemical reagents until the disappearance of the blue color based on the analysis methods of American Oil Chemist's Society [14]. IV was calculated by the following Eq. 1:

$$\text{Iodine value} = (B-S) \times N \times 0.001269/W \quad 1$$

where S and B are the amounts (in unit of mL) of sodiumthiosulfate titrated for 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, density 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 D445, ASTM D 93 (Pensky–Martens Flashpoint Apparatus, Lazer Scientific Inc., Germany), ASTM D 2500 and ASTM D 97 respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of castor oil

The various properties of extracted castor oil was measured by standard method and presented in Table1.

Table 1: Properties of raw castor oil.

Property name	Value
Specific gravity at 25°C	0.95
Kinematic viscosity (mm <sup>2</sup> /s ) at 40°C	253
FFA content (%)	27.8
Moisture content (%)	0.1
Saponification value (mg of KOH/gm of oil)	232.05
Iodine value ( g I <sub>2</sub> /100 g oil)	79.3
Color	Pale yellow
*Molecular Weight (gm/mol)	876.92

\*Molecular weight was determined from composition of the oil.

### 3.2 Preparation of biodiesel from castor oil by three-step method

#### 3.2.1. Preparation of FFA

FFA was prepared from oil by saponification reaction followed by acidification. Saponification reaction was conducted with aqueous sodium hydroxide solution. Saponification reaction was carried out with different stoichiometric molar amount of sodium hydroxide. The results are represented in Figure: 1. From Figure 1. It can be seen that, the optimum molar ratio of oil to NaOH was 1:2 and reaction time was 2.5 h.

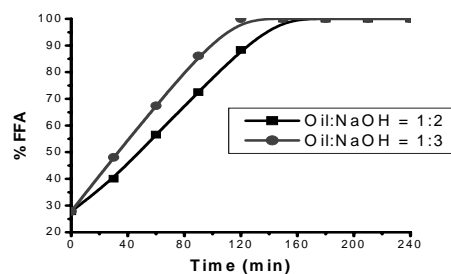


Fig. 1: Preparation of FFA from castor oil through saponification and acidification by different stoichiometric molar amount of sodium hydroxide to oil in aqueous solution [Reaction temperature = 100°C under reflux with vigorous stirring].

### 3.2.2 Preparation of biodiesel from FFA

The methanol/FFA molar ratio is one of the important variables that affect the FFA conversion to biodiesel. From the reaction stoichiometry 1 mole alcohol is required for 1mole of FFA to convert biodiesel. The effect of methanol molar ratio on the conversion of FFA to biodiesel is represented in the Figure 2.

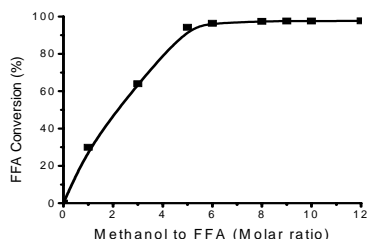


Fig. 2: Effect of Methanol/FFA molar ratio on FFA conversion to biodiesel. [Reaction temperature = 60°C, catalyst (H<sub>2</sub>SO<sub>4</sub>) concentration 5wt% of FFA and reaction time 2 h under reflux with vigorous stirring].

From the Figure. 2 it was observed that, the FFA conversion increases as the molar ratio of Methanol/FFA increases. The conversion was 97.4% at the molar ratio of FFA to methanol 1:9. Further increase in the FFA to methanol molar ratio, conversion does not increase. The optimum molar ratio of FFA to methanol was 1:9.

Effect of catalyst concentration on esterification was investigated and the results are presented in Figure 3.

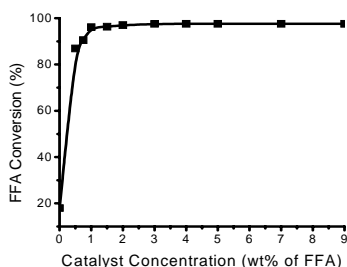


Fig. 3: Effect of catalyst concentration on esterification reaction [Reaction temperature = 60°C, FFA / methanol molar ratio 1:9, Reaction time 2 h with vigorous stirring ].

From the Figure 3 it can be seen that, maximum conversion of FFA was 97.4% obtained at catalyst (H<sub>2</sub>SO<sub>4</sub>) concentration of 5wt% to FFA. Further increase in catalyst concentration does not increase the conversion. The optimum catalyst concentration was 5 wt% of H<sub>2</sub>SO<sub>4</sub> to FFA.

Effect of temperature in esterification reaction was investigated and the results are presented in Figure 4. From Figure 4 it was observed that, the highest conversion was found at a temperature of 60°C.

Further increase in temperature conversion remain unchanged. The optimum temperature for esterification reaction was 60°C.

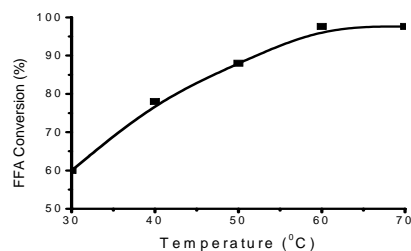


Fig. 4: Effect of Temperature on esterification reaction [Catalyst (H<sub>2</sub>SO<sub>4</sub>) concentration 5 wt% of FFA, FFA / methanol molar ratio 1:9 and reaction time 2 h under reflux with vigorous stirring].

### 3.3 Optimum reaction parameters for three-step method

The optimum reaction parameters for three-step methods of biodiesel preparation from castor oil are presented in Table 2.

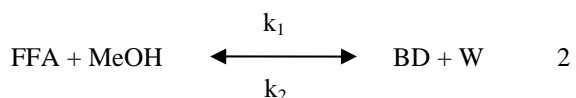
Table 2: Optimum reaction parameters for three-step method.

Step	Parameters	Value
Saponification	Molar ratio of oil to NaOH	1:2
	Reaction Time	2.5 h
Acidification	Molar ratio of Soap to HCl	1:1.5
Esterification	Molar ratio of FFA to Methanol	1:9
	Reaction Temperature	60 °C
	Catalyst (H <sub>2</sub> SO <sub>4</sub> ) concentration	5 wt% to FFA
	Reaction time	2.0 h

### 3.4 Esterification kinetics at different temperature

The Esterification reaction was carried out at 1:9 molar ratio of methanol to FFA and 5 wt% of catalyst to FFA at different temperature. Sample was taken at different time interval and the reduction of FFA was analyzed. The results are presented in Fihgure 5.

The esterification reaction can be written as



Where, FFA is free fatty acid, MeOH is methanol, BD is biodiesel and W is water.  $k_1$  is the forward reaction rate and  $k_2$  is the backward reaction rate. From the reaction, the equilibrium constant is

$$K = \frac{C_{BDe} C_{We}}{C_{FFAe} C_{MeOHe}} = \frac{k_1}{k_2} \quad 3$$

Where  $C_{BDe}$ ,  $C_{We}$ ,  $C_{FFAe}$  and  $C_{MeOHe}$  is the equilibrium concentration of biodiesel, water, FFA and methanol respectively. The value of equilibrium constant can be determined experimentally and the value was,  $K=1.832$

According to stoichiometry of the above reaction, the overall reaction rate can be written as,

$$\frac{dC_{FFA}}{dt} = -k_1 C_{FFAt} C_{MeOHt} + k_2 C_{BDt} C_{Wt} \quad 4$$

Where  $C_{BDt}$ ,  $C_{Wt}$ ,  $C_{FFAt}$  and  $C_{MeOHt}$  are the concentration of biodiesel, water, FFA and methanol at time  $t$  respectively.

Let, the conversion of the reaction is  $X$

Equation (4) can be written in terms of conversion as follows:

$$\begin{aligned} C_{FFA0} \frac{dX_t}{dt} &= k_1 C_{FFA0} (1-X) C_{FFA0} (\theta_B - X) \\ &\quad - k_2 C_{FFA0} (\theta_C + X) C_{FFA0} (\theta_D + X) \\ \Rightarrow \frac{dX_t}{dt} &= k_1 C_{FFA0} (1-X) (\theta_B - X) \\ &\quad - \frac{k_1}{K} C_{FFA0} (\theta_C + X) (\theta_D + X) \end{aligned} \quad 5$$

Where,  $\theta_B = C_{MeOH}/C_{FFA0}$ ,  $\theta_C = C_{BD}/C_{FFA0}$  and  $\theta_D = C_W/C_{FFA0}$ .

By solving this equation (5) we get,

$$X = \alpha \left\{ \frac{\frac{\beta}{\alpha} e^{(\alpha-\beta)k_1 t} - 1}{e^{(\alpha-\beta)k_1 t} - 1} \right\} \quad 6$$

Where,  $\alpha = \frac{b + \sqrt{b^2 - 4ac}}{2a}$ ,  $\beta = \frac{b - \sqrt{b^2 - 4ac}}{2a}$ ,  
 $a = C_{FFA0} \left(1 - \frac{1}{K}\right)$ ,  $b = C_{FFA0} (1 + \theta_B)$  and  
 $c = C_{FFA0} \theta_B$

From equation (6) we get,

$$\frac{1}{(\alpha - \beta)} \ln \left( \frac{X - \alpha}{X - \beta} \right) = k_1 t \quad 7$$

A plot of  $\frac{1}{(\alpha - \beta)} \ln \left( \frac{X - \alpha}{X - \beta} \right)$  vs.  $t$  represents a straight line of slope  $k_1$ .

Experimental data was fitted in equation (7) and the forward reaction rate was evaluated and the value was  $0.051 \text{ min}^{-1}$ . By using the value of  $k_1$  in equation (6) we can find the theoretical conversion of FFA

with respect to time. A Plot of FFA conversion (theoretical and experimental) vs. time was shown in the Figure 6. By using the value of equilibrium constant and forward rate we can find out, the backward reaction rate and the value was  $k_2 = 0.0278 \text{ min}^{-1}$ .

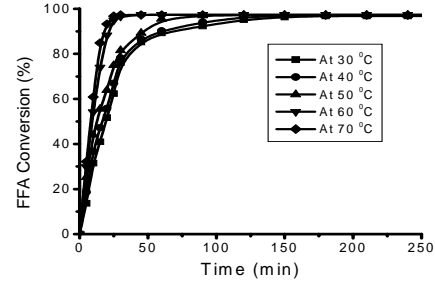


Fig. 5: Kinetics study of esterification at different temperature [FFA/Methanol molar ratio = 1:9 and catalyst ( $H_2SO_4$ ) concentration 5 wt% of FFA under reflux with vigorous stirring].

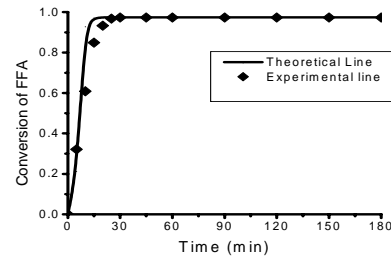


Fig. 6: conversion of FFA-Time curve for esterification reaction (Dense line-theoretical, Points-experimental). [Reaction temperature =  $60^\circ\text{C}$ , oil/methanol molar ratio 1:9 and Catalyst concentration 5% wt. of FFA under reflux with vigorous stirring.]

### 3.5 Final properties of biodiesel

Biodiesel was prepared at optimum condition from the castor oil. Various properties of the biodiesel was measured and it is compared with the standard biodiesel and diesel properties and presented in Table 3. The viscosity and specific gravity of the produced biodiesel was higher than biodiesel standard. This biodiesel was blended with petro-diesel with different volumetric proportion. The results are presented in Figure 7. From the figure it can be seen that the mixture of 70% biodiesel and 30% petro-diesel by volume named B70 can be safely used in diesel engine.

## 4 CONCLUSION

Biodiesel was prepared from castor oil by three-step method. The reaction parameters for saponification,

acidification and esterification were optimized. The viscosity of the oil was reduced from 252.32 mm<sup>2</sup>/s to 14.6 mm<sup>2</sup>/s and the FFA content was reduced from 27.8 wt% to 2.6%. The property of the produced biodiesel are not match with the biodiesel standard. This is occur because the raw oil contains higher FFA content and its viscosity also high. 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 properties of B70 are similar with biodiesel. This product can be successfully used as diesel in diesel engine.

Table 3: Properties of biodiesel.

Properties	Experimental value	Biodiesel Standard [15,16]	Diesel Standard
Viscosity mm <sup>2</sup> /s at 40°C	14.6	1.9–6.0	1.3 – 4.1
Specific gravity at 25 °C (kg/m <sup>3</sup> )	0.90	0.88 (at 15.5 °C)	0.85 (at 15.5 °C)
Flash point (°C)	180	100 to 170	60 to 80
Cloud point (°C)	3	-3 to 12	15 to 5
Pour point (°C)	6	15 to 10	-35 to -15
FFA Weight%	2.6	Trace	-
Copperstrip corrosion	Non-corrosive	-	-
Calorific Value(Mj/Kg)	36.25	-	42

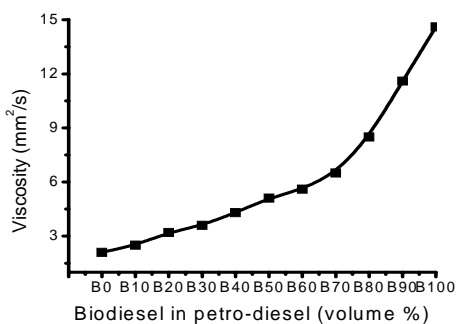


Fig. 7: blending curve of biodiesel with petro-diesel.

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