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Optimization of Three-Step Method For Biodiesel Production From Waste Cook Oil

Kaniz Ferdous[1*], M. Rakib Uddin[1], M. Rahim Uddin[1], Maksudur R. Khan[1, 2,], M. A. Islam[1]

[1]Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology (SUST), Sylhet 3114, Bangladesh.

[2]Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia.

Abstract

In this paper, production of biodiesel from Waste Cook Oil (WCO) by three-step method and optimization of the process were studied. The properties of raw oil were measured by standard methods. The raw oil containing 1.9 wt% Free Fatty Acid (FFA) and viscosity was 54.53 mm^2/s. Biodiesel was prepared from WCO by three-step method. In the three-step method, the first step was saponification of the oil followed by acidification to produce FFA and finally esterification of FFA to produce biodiesel. The reaction parameters in saponification, acidification and esterification reaction were optimized. Silica gel was used during esterification reaction to adsorb water produced in the reaction and silica gel to FFA ratio was 1.5:10 wt/wt. Hence the reaction rate was increased and finally the FFA was reduced to 0.98 wt%. A factorial design was studied for esterification reaction to obtain the higher yield of biodiesel. Finally various properties of biodiesel such as FFA, viscosity, specific gravity, cetane index, pour point, flash point etc. were measured and compared with biodiesel and petro-diesel standard.

1. INTRODUCTION

Diesel oil, generated from petroleum by refining, is an important fuel for many engines. Combustion of diesel produces carbon dioxide, which is assumed to contribute to the global warming. Furthermore, mineral fuels contain sulfur, which, if not removed prior to combustion, is a cause of acid rain. The discussion on reduction of CO_2 emissions and on high prices for fossil diesel fuel leads to an enforced search for production of fuels from renewable sources. In the announcements of the EU-committee, the intention to replace 5.8% fossil diesel fuel with fuel from biogeneous sources [1].

Biodiesel, a mixture of fatty acid methyl esters (FAME), is a clean-burning fuel derived from vegetable oils or animal fat and is an advantageous alternative to fossil diesel fuel because of its biodegradability, biorenewable nature, very low sulfur content and toxicity, low volatility or flammability, good transport and storage properties, higher cetane number, and its salutary atmospheric CO_2 balance for production [2]. In Bangladesh the potentiality of producing oil source was investigated and it was found that the production potential was not too high. As we have a very large population, the edible oil sources cannot be employed for the biodiesel production. Moreover we have extreme limitation of land. So additional land acquiring is also impossible for the production of oil seeds. The oil seed source that can be used for biodiesel production in Bangladesh are WCO, mustard oil, sesame oil, coconut oil, peanut oil, linseed oil, castor oil, nahor oil etc. [3].

The high cost of biodiesel is mainly due to the cost of virgin vegetable oil. Therefore, it is not surprising that the biodiesel produced from vegetable oil (for example, pure soybean oil) costs much more than petroleum based diesel. Therefore, it is necessary to explore ways to reduce production costs of biodiesel. In this sense, methods that permit minimizing the costs of the raw material are of special interest. The use of waste frying oil, instead of virgin oil, to produce biodiesel is an effective way to reduce the raw material cost because waste frying oil is estimated to be about half the price of virgin oil [4].

There are different methods for biodiesel preparation like base or acid catalyzed transesterification [5,6], two step method [7] and three-step method [8]. Encinar et. al., (2005) [9] prepared biodiesel from WCO by base catalyzed transesterification but the reaction yield was too low than two-step method was conducted to increase the reaction yield, Zheng et. al., (2006) [4] produced biodiesel from WCO by acid catalyzed transesterification but the molar ratio of oil to methanol was 1:74. In this method huge amount methanol required for reaction and additional cost involved for the separation of biodiesel. In the present study biodiesel was prepared from WCO by three-step method to increase the reaction yield and minimize the methanol molar ratio. Additionally optimization study was done by the application of factorial design to find out the better reaction conditions.

2. MATERIALS AND METHODS

2.1 Chemicals

Methanol (99-100%), ethanol (99-100%), calcium oxide (CaO), sodium hydroxide pellets (96%), potassium hydroxide pellets (>84%), phenolphthalein (pH 8.2-9.8),

acetone (99%), diethyl ether , hydrochloric acid (37%), sulfuric acid (98%), iodine , sodium iodide, bromine, carbon tetrachloride, glacial acetic acid, potassium dichromate etc. All the chemicals were used as analytical reagent grade.

2.2 Raw materials

WCO (palm oil and soybean oil) was collected from local restaurants located in Sylhet city in Bangladesh. The oil was filtered and its properties were measured.

2.3 Biodiesel preparation by Three- step method

For saponification process required amount of WCO was taken in a three necked flask and mixed with different stoichiometric amount of aqueous calcium oxide solution [8]. The mixture was heated under reflux with vigorous stirring at temperature of 100 ^{0}C for different time. After saponification, produced calcium soap solution was treated with different stoichiometric amount of concentrated hydrochloric acid at a temperature of 65 -70 ^{0}C. After dissolving the soap, the fatty acid contents were separated in separatory funnel. Hot water wash was given for removing mineral acid from the fatty acid. The FFA content was determined by titration method. When acidification was completed, produced FFA was reacted with different stoichiometric amount of methanol under reflux with vigorous stirring at different temperature, catalyst concentration, different molar ratio of methanol to FFA and different time. All the reaction parameters were optimized. Silica gel was used during esterification reaction to adsorb water produced in esterification reaction. After preparing the biodiesel from WCO various physico-chemical properties were measured and compared with the biodiesel and petro-diesel standard.

2.4 Analytical methods for oil and biodiesel

To determine FFA of sample and biodiesel, 1mL of oil and biodiesel were weighed in gm , then dispersed in 5mL diethyl-ether solution followed by titration against 0.1 M KOH [10]. Saponification value (SV) was determined by method described by Jeffery et al., (1991) [10].To determined S.V. 2 gm sample was taken in 50 mL alcoholic KOH then heated at 65 °C with vigorous stirring for 30 min and titrated against 0.5 M hydrochloric acid. The iodine value (IV) were determined by titrating 0.01 N sodium thiosulfate 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 [11]. IV was calculated by
the following equation (1).

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

where, S and B are the amounts (in unit of mL) of sodium thiosulfate titrated for the tested sample and blank sample respectively; N is the molar concentration (in unit of mol/L) of sodium thiosulfate and W is the weight (in unit of gm) of the tested sample.
Physical properties color, moisture content and density of the sample were by the following ASTM D 1500, ASTM D 1744 (Karl fisher method), ASTM D 1480/81 and ASTM D 240. Viscosity, cloud point, pour point were determined by standards ASTM D445 respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of WCO

The properties of WCO such as viscosity, specific gravity, moisture content, saponification value, pour point, cloud point etc were measured and presented in Table 1.

Table 1. Properties of WCO

Properties	Experimental value
Physical state	Liquid
Color	Deep oily
Specific gravity at 25^{0}C	0.90
Kinematic viscosity, mm^2/s at 40 ^{0}C	54.53
FFA content (wt% of oil)	1.9
Average molecular weight of FFA (gm/mol)	275.5
Molecular weight of oil (gm/mol)	864.5
Saponification value (mg of KOH/gm of oil)	238
Cloud point (^{o}C)	12
Pour point (^{o}C)	6

3.2 Biodiesel prepared by three-step method

3.2.1 FFA preparation: FFA was prepared from WCO by saponification followed by acidification. Saponification was done by the method described above. Saponification was done with different stoichiometric amount of CaO. After saponification and acidification FFA was produced.

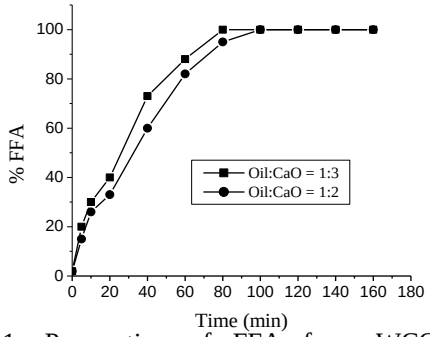

Fig. 1: Preparation of FFA from WCO through saponification and acidification in aqueous solution

[Reaction temperature = 100 ^{0}C under reflux with vigorous stirring].
The results are present in Fig. 1. From the Fig. 1 it can be seen that, the optimum molar ratio of oil to CaO was 1:2 and reaction time was 120 min.

3.2.2 Biodiesel Preparation from FFA: The methanol to FFA molar ratio, catalyst concentration, temperature and silica gel dosages are the important parameters that affecting the FFA conversion to biodiesel. The effect of methanol to FFA molar ratio, catalyst concentration, temperature and amount of silica gel on conversion of FFA was investigated. The results are shown in Fig. 2,3,4,5.From the Fig. 2,3,4, it was found that the FFA conversion to biodiesel was 98% at 6:1 molar ratio of methanol to FFA, 5 wt% catalyst (HCl) concentration, 60 ^{o}C temperature. From the Fig. 5, it can be seen that 98% conversion was achieved within 80 minutes in presence of silica gel and reaction rate was increased.

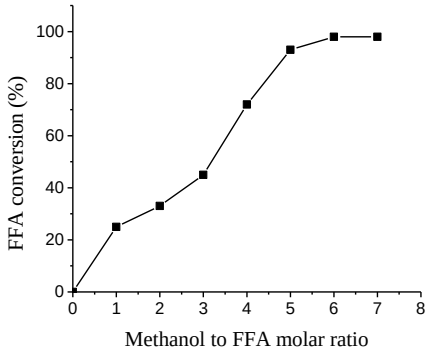

Fig. 2: Effect of Methanol to FFA molar ratio on FFA conversion [temperature 60 ^{o}C, catalyst (HCl) 5 wt% of FFA, time 120 min under reflux with vigorous stirring].

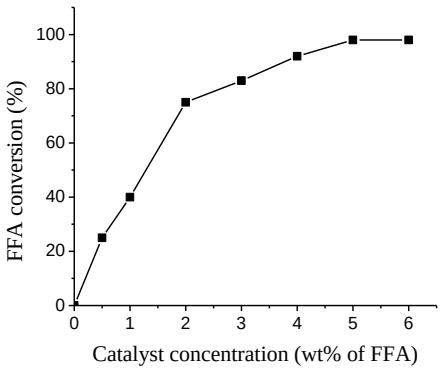

Fig. 3: Effect of catalyst (HCl) concentration on esterification reaction [Reaction temperature 60 ^{0}C, methanol to FFA ratio 6:1, Reaction time 120 min, under reflux with vigorous stirring].

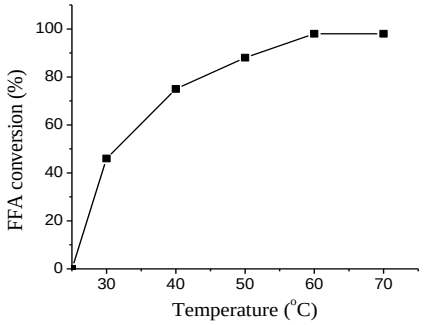

Fig. 4: Effect of Temperature on esterification reaction [Catalyst (HCl) concentration 5 wt% of FFA, methanol to FFA molar ratio 6:1, Reaction time 120 min, under reflux with vigorous stirring].

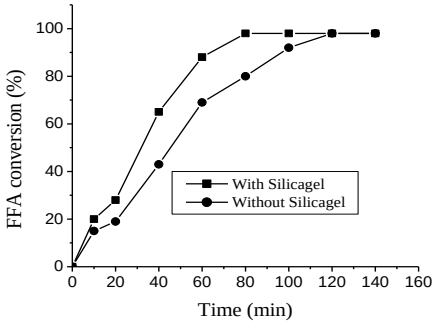

Fig. 5: Conversion of FFA to biodiesel at different methanol to FFA molar ratio in absence and presence of silica gel [Reaction temp. 60 ^{0}C and Catalyst (HCl) concentration 5.0% wt of FFA under reflux with vigorous stirring].

3.3 Optimization study

Four factors (methanol to FFA molar ratio, catalyst concentration, temperature and reaction time) affect the biodiesel production process from WCO. To study the optimization of process, a factorial design was carried out. The experiments were carried out according to half-Replicate of 2^4 full factorial design. Table 2 shows the decoding values for methanol to FFA molar ratio, catalyst concentration, reaction temperature and reaction time. Eight set of experiments were run for the factorial design and the results are shown in Table 3. Table 4 presents the values of sample variances.

Table 2. Decoding values of independent variables used in the experimental design

Factors	Max. (+1)	Min. (-1)
Molar ratio (X_1)	8	3
Catalyst conc. (X_2)	6	2
Temperature, °C (X_3)	60	40
Time (min) (X_4)	90	30

Table 3. Design of the experiment using coded value

No. of runs	X_o	X_1	X_2	X_3	X_4	Y_1	Y_2	Y_3	Y_4	Y_5	$\bar{Y}$	S_i^2
1	+1	+1	+1	+1	+1	98.3	98.98	97.49	97.03	99.04	98.17	0.80
2	+1	+1	+1	-1	-1	75.28	77.99	74.62	77.87	77.67	76.69	2.58
3	+1	+1	-1	+1	-1	94.13	93.12	96.09	93.07	95.06	94.30	1.68
4	+1	+1	-1	-1	+1	93.84	91.76	94.02	91.65	90.52	92.36	2.30
5	+1	-1	+1	+1	-1	90.62	91.94	91.51	92.84	90.12	91.40	1.16
6	+1	-1	+1	-1	+1	74.15	72.07	73.99	73.96	71.78	73.20	1.35
7	+1	-1	-1	+1	+1	86.73	84.10	84.23	87.32	85.57	85.60	2.10
8	+1	-1	-1	-1	-1	75.62	76.13	76.50	75.97	78.37	76.52	1.16
											$\sum\bar{Y}$ = 688.24	$\sum S_i^2$= 13.13

Table 4. Sample Variances

S_1^2	0.80	S_5^2	1.16
S_2^2	2.58	S_6^2	1.35
S_3^2	1.68	S_7^2	2.10
S_4^2	2.30	S_8^2	1.16

Where Y is the conversion of FFA to biodiesel in esterification reaction and $\bar{Y}$ is average value of Y. The sample variances were determined and tested for homogeneity on the basis of Cochran's criterion. It was found that the sample variances are homogeneous for the significance level $\alpha = 0.05$ and the number of degrees of freedom $\nu_1 = 4$ and $\nu_2 = 8$ and the error mean square was 1.65.The complete regression equation describes the contributions of the various factors on the outcome (response) of the biodiesel conversion.

$$\hat{Y} = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_{12} + b_{13}X_{13} + b_{23}X_{23} \quad (2)$$

The coefficients of the regression equation were estimated and the significance of the coefficients was tested using the student T-test. Only one coefficient appeared as insignificant for the significance level $\alpha = 0.01$. Neglecting the insignificant coefficient the final regression equation becomes as:

$$\hat{Y} = 86.03 + 4.34X_1 - 1.16X_2 + 6.53X_3 + 1.29X_4 - 1.78X_{12} + 3.58X_{23} \quad (3)$$

Using the Fisher's test the adequacy fitness of the regression equation was determined. With $\alpha = 0.01$, $\nu_1 = 1$ and $\nu_2 = 32$ the tabulated value of Fisher's F was 7.5 where as our experimental value was 5.66. Therefore the equation fits in the experiment.

3.4 Properties of biodiesel

The properties of produced biodiesel such as viscosity, FFA content, moisture content, pour point, cloud point, saponification value, iodine value, specific gravity were presented in Table 5 and compared with standard biodiesel and petro-diesel values. The reaction yield was 78%.

Table 5. Properties of biodiesel produced from WCO by three-step method and comparison with standard biodiesel and petro-diesel values.

Properties	Produced biodiesel value	Biodiesel Standard [8.12]	Petro-Diesel standard [12]
Specific gravity, at 25 ^oC	0.811	0.88 (at 15.5^0 C)	0.85(at 15.5^0 C)
Kinematic viscosity (mm^2/s), at 40^oC	3.93	1.9–6.0	1.3 – 4.1
FFA content (wt%)	0.98	-	-
Moisture content (vol%)	0.10	0.05% max.	0.161
Saponification value (mg KOH/gm oil)	187	-	-
Flash point (^{0}C)	150	100 to 170	60 to 80
Iodine value	84	-	-
Cloud point (^{o}C)	2	-3 to 12	-15 to 5
Pour point (^{o}C)	0	-15 to 10	-35 to -15

4. CONCLUSION

Biodiesel was prepared from WCO by three-step method, in three-step method aqueous calcium oxide solution was used for saponification, the molar ratio of oil to CaO and reaction time were optimized. The optimum molar ratio for saponification by aqueous calcium oxide was 1:2 oil to CaO and reaction time was 120 min at 100 ^{0}C. In acidification the molar ratio of soap to hydrochloric acid was 1:2 for calcium soap. In Esterification the optimum molar ratio of methanol to FFA was 6:1, the catalyst (HCl) concentration was 5 wt% of FFA, the reaction temperature was 60 ^{0}C and the reaction time was 120 min, with silica gel reaction time was reduced to 80 min and FFA content was reduced to 0.98 %. A factorial design was applied to find the optimum conditions for esterification reaction. At optimum conditions 98% conversion of the FFA to FAME was obtained. The properties of produced biodiesel such as viscosity, specific gravity, cloud point, pour point, flash point are nearest to the petro-diesel. The present experimental results support that produced biodiesel from WCO by this method can be successfully used as diesel.

5. REFERENCES

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6. NOMENCLATURE

Symbol	Meaning	Unit
M	Molarity	Mol/L
N	Normality	Equivalent mol/L