Synthesis of Biodiesel from Waste Cooking Oil

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Abstract In the present study biodiesel was synthesized from Waste Cook Oil (WCO) by three-step method and regressive analyzes of the process was done. The raw oil, containing 1.9wt% Free Fatty Acid (FFA) and viscosity was 47.6mm^2/s. WCO was collected from local restaurant of Sylhet city in Bangladesh. Transesterification method gives lower yield than three-step method. In the three-step method, the first step is saponification of the oil followed by acidification to produce FFA and finally esterification of FFA to produce biodiesel. In the saponification reaction, various reaction parameters such as oil to sodium hydroxide molar ratio and reaction time were optimized and the oil to NaOH molar ratio was 1:2, In the esterification reaction, the reaction parameters such as methanol to FFA molar ratio, catalyst concentration and reaction temperature were optimized. Silica gel was used during esterification reaction to adsorb water produced in the reaction. Hence the reaction rate was increased and finally the FFA was reduced to 0.52wt%. A factorial design was studied for esterification reaction based on 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. The reaction yield was 79%.

Keywords: saponification, acidification, esterification, factorial design, biodiesel

1. Introduction

Due to the predicted shortness of conventional fuels and environmental concerns, a search for alternative fuels has gained recent significant attention. As the calorific value of vegetable oils is comparable to that of diesel, they could be used as fuels in compression ignition engines [1]. The diesel engine is widely used to provide the power source on-land transportation vehicles, marine vessels and power plants. However, a diesel engine also emits various forms of pollutants in gaseous, liquid and solid phases to the environment. These pollutants can endanger human health and damage the ecological environment [2].The concern is increasing worldwide for environmental protection and for the conservation of non-renewable natural resources. Fatty acid methyl esters (FAME) show great potential as diesel substitutes, and they are known to be sources of biodiesel [3].

Biodiesel (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, bio-renewable 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 [4]. Treatments that circumvent the significant problems associated with the high viscosity of plant oils when used as engine fuels are its dilution, micro emulsification, pyrolysis, and transesterification with methanol; the latter

approach is used most commonly. The glycerin formed during transesterification is also important because of its numerous applications in the food, cosmetic, and pharmaceutical sectors. FAME is not only currently useful as a diesel fuel additive, but it is also marketed as green industrial degreasing solvents; as diluents for pigments, paints, and coatings, and for military engine fuel applications [4].

Currently, more than 95% of the world biodiesel is produced from edible oil which is easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oil has recently been a great concern because they compete with food materials – the food versus fuel dispute [5]. There are concerns that biodiesel feedstock may compete with food supply in the long-term. Non-edible plant oil has been found to be promising crude oil for the production of biodiesel. The use of non-edible oil for biodiesel production compared with edible oil is very significant in developing countries because of the tremendous demand of edible oil as food and they are far too expensive to be used as fuel at present [5,6].

In Bangladesh the potentiality of producing oil source is investigated and it is found that the production potential is 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. [7].

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 [8].

There are different methods for biodiesel preparation like base or acid catalyzed transesterification [9,10], two step method [11] and three-step method [12]. Encinar et. al [13] prepared biodiesel from WCO by base catalyzed transesterification but the reaction yield was too low then two-step method was conducted to increase the reaction yield. Zheng et. al [8] 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 regressive analyzes study was done by the application of factorial design based on viscosity to find out the better reaction conditions.

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), acetone (99%), diethyl ether , hydrochloric acid (37%), 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

Waste cook oil (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. Preparation of Biodiesel by Three-step Method

Three-step method consists of Saponification followed by acidification to produce FFA and finally esterification of FFA to produce biodiesel [12].

2.3.1. Saponification

For saponification process required amount of WCO was taken in a three necked flask and mixed with different stoichiometric amount of aqueous sodium hydroxide solution. The mixture was heated under reflux with vigorous stirring at temperature of 100°C for different time. The reaction was stopped by cooling the reaction volume. Aqueous sodium hydroxide solution was prepared by dissolving required amount of dry sodium hydroxide (NaOH) in 60-90ml water. The reaction time and different molar ratio of oil to sodium hydroxide solution through saponification process were optimized.

2.3.2. Acidification

After saponification, produced sodium soap solution was treated with different stoichiometric amount of concentrated hydrochloric acid at a temperature of 65-70°C under reflux with vigorous stirring. After dissolving the soap, the fatty acid contents were separated in separatory funnel. After separation, hot water wash was given for removing mineral acid from the fatty acid. The FFA content was determined by titration method. The different molar ratio of soap to hydrochloric acid was given and the ratio was optimized.

2.3.3. Esterification of FFA

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 standard biodiesel. The yield of biodiesel was calculated by the following equation:

$$Yield = \frac{W(biodiesel)}{W(Oil)} \qquad (1)$$

where, W(biodiesel) is the weight of produced biodiesel and W(oil) is weight of oil.

2.4. Analytical Methods for Oiul 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 by the method described in AOCS Aa 6-38. Saponification value (SV) was determined by method described by Jeffery et al. [14]. To determined S.V. 2gm sample was taken in 50mL alcoholic KOH then heated at 65°C with vigorous stirring for 30min and titrated against 0.5M hydrochloric acid [14]. The iodine value (IV) was determined by titrating the sample with 0.01 N sodium thiosulphate and chemical reagents until the disappearance of blue color. Iodine value was calculated by following equation:

$$IV = \frac{(V_1 - V_2) * S * 0.126 * 100}{W} \qquad (2)$$

where, V_1 and V_2 are the volume of sodium thiosulphate (mL) required for titration with sample and blank titration, S is the concentration of $Na_2S_2O_3$ in Normality, W is the

weight of oil sample in gm. 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.

3.2. Preparation of FFA from WCO

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 NaOH. After saponification and acidification FFA was produced. The results are represent 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 2.0h.

Table 1. properties of WCO

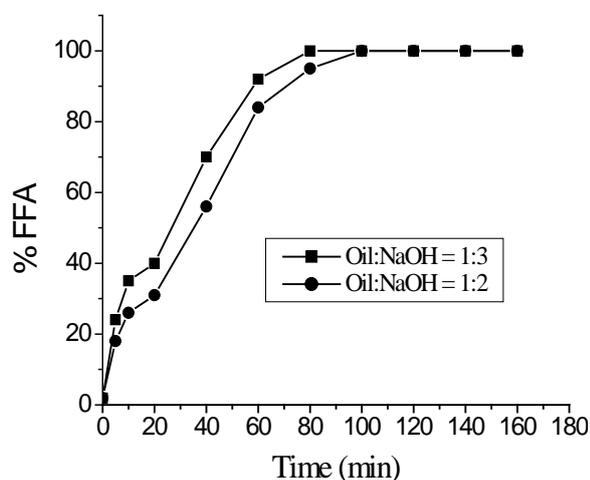| Properties	Experimental value
Physical state	Liquid
Color	Deep oily
Specific gravity at 25°C	0.902
Kinematic viscosity, mm^2/s at 40°C	54.53
FFA content (wt% of oil)	1.9
Average molecular weight of FFA (gm/mol)	275.5
Molecular weight of oil (gm/mol)	864.5
Saponification value (mg of KOH/gm of oil)	238
Cloud point (°C)	12
Pour point (°C)	6

Figure 1. Preparation of FFA from WCO through saponification and acidification

3.3. Preparation of Biodiesel from FFA

3.3.1. Effect of Methanol to FFA Molar Ratio

The methanol to FFA molar ratio is one of the important parameter that affecting the FFA conversion to biodiesel. The effect of methanol to FFA molar ratio on conversion of FFA was investigated at fixed temperature and catalyst concentration. The results are represented in Figure 2. From the Figure 2, it was found that the FFA conversion to biodiesel was 98% at 6:1 molar ratio of methanol to FFA. Further increase in methanol to FFA molar ratio conversion does not increase. The optimum molar ratio of methanol to FFA was 6:1.

3.3.2. Effect of Catalyst Concentration on Esterification

Catalyst concentration has a significant role on conversion of FFA to methyl ester. Increase of catalyst concentration increases the percentage of FFA conversion. At a certain catalyst concentration the conversion was higher. HCl was used as catalyst. The effect of catalyst concentration on conversion of FFA was investigated the results are represented in Figure 3. From the Figure 3, it can be seen that the conversion was 98% at the catalyst concentration of 5 wt% of FFA. Further increasing the catalyst concentration conversion does not increase. The optimum catalyst concentration was 5 wt% of FFA.
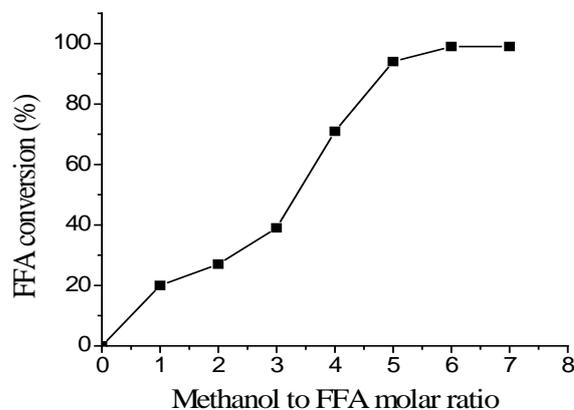

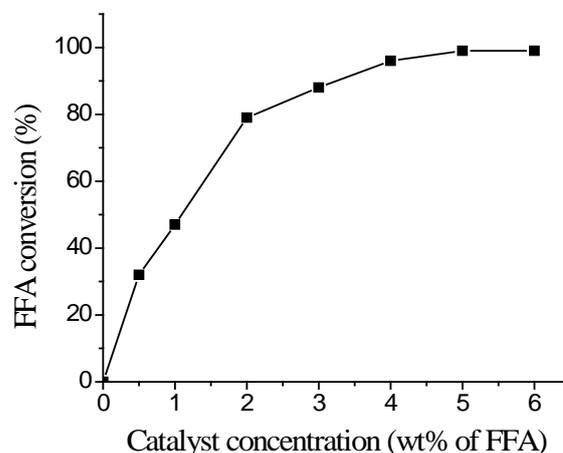**Figure 2.** Effect of Methanol to FFA molar ratio on FFA conversion

3.3.3. Effect of Silica Gel on Esterification Reaction

Silica gel adsorbs the water produced in esterification reaction. Hence increase the reaction rate. The effect of silica gel was studied in esterification reaction by taking 5 gm silica gel for 50g FFA. Further increasing of silica gel, the conversion remains unchanged. The results are presented in Figure 4. From the Figure 4, it can be seen that more than 99% conversion in terms of FFA content was achieved within 80 minutes and reaction rate was increased.
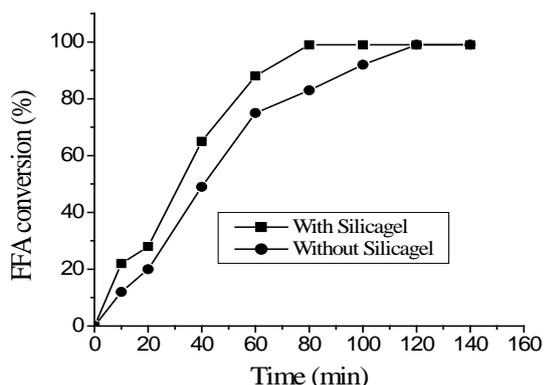

Figure 4. Effect of silica gel in esterification reaction

3.3.4. Effect of Temperature

Temperature has a significant effect on conversion of FFA to methyl ester. By increasing temperature %FFA conversion was increased. At a certain temperature the conversion was higher. The effect temperature on conversion of FFA was investigated the results are represented in Figure 5. From the Figure 5, it can be seen that the conversion was 98% at 60°C temperature. Further increasing of temperature the percentage FFA conversion does not increase. The optimum temperature was 60°C.

3.4. Regressive Analyzes of Esterification Reaction

Four factors (methanol to FFA molar ratio, catalyst concentration, temperature and reaction time) affect the biodiesel production process from WCO. To study the regressive analyzes of Esterification reaction, a factorial design was carried out. The experiments were conducted 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.
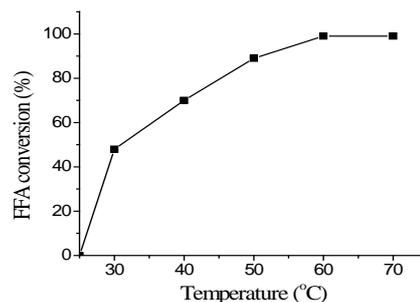

Figure 5. Effect of Temperature on esterification reaction

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	$\overline{Y}$	S_i^2
1	+1	+1	+1	+1	+1	74	76	76.8	76.5	77	76.06	1.46
2	+1	+1	+1	-1	-1	65	66	64	68	66.5	65.9	2.3
3	+1	+1	-1	+1	-1	70	68	69	71	72	70	2.5
4	+1	+1	-1	-1	+1	72	74	74.5	74	74	73.7	0.95
5	+1	-1	+1	+1	-1	68	68	66.5	65	65	66.5	2.25
6	+1	-1	+1	-1	+1	74	73	73	75.5	72	73.5	1.75
7	+1	-1	-1	+1	+1	70	71.5	72.2	73	71	71.54	1.30
8	+1	-1	-1	-1	-1	62	60	61	64	64	62.2	3.2
											$\sum \overline{Y} = 559.4$	$\sum S_i^2 = 15.72$

Where Y is the yield of biodiesel and $\overline{Y}$ 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 $v1 = 4$ and $v2 = 8$ and the error mean square was 1.96.

Table 4. Sample Variances

S_1^2	1.46	S_5^2	2.25
S_2^2	2.3	S_6^2	1.75
S_3^2	2.5	S_7^2	1.30
S_4^2	0.95	S_8^2	3.2

The complete regression equation describes the contributions of the various factors on the outcome (response) of the biodiesel conversion.

$$\hat{Y} = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 \\ + b_{12}X_{12} + b_{13}X_{13} + b_{23}X_{23} \quad (3)$$

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

Neglecting the insignificant coefficient the final regression equation becomes as:

Using the Fisher's test the adequacy fitness of the regression equation was determined. With $\alpha = 0.01$, $\nu_1 = 3$ and $\nu_2 = 32$

$$\hat{Y} = 69.9 + 1.49X_1 + 1.1X_3 \\ + 3.77X_4 - 1.03X_{12} \quad (4)$$

the tabulated value of Fisher's F was 4.5 where the experimental value was 3.96. 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 etc. were presented in Table 5 and compared with standard values. The reaction yield was 79%.

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

Properties	Produced biodiesel value	Biodiesel Standard [12,15]	Diesel standard [15]
Specific gravity, at 25°C	0.792	0.88 (at 15.5°C)	0.85(at 15.5°C)
Kinematic viscosity (mm^2/s), at 40°C	3.29	1.9–6.0	1.3 – 4.1
FFA content (wt%)	0.94	-	-
Moisture content (%)	0.12	0.05% max.	0.161
Saponification value	194	-	-
Flash point (°C)	150	100 to 170	60 to 80
Iodine value	88	-	-
Cloud point (°C)	0	-3 to 12	-15 to 5
Pour point (°C)	-3	-15 to 10	-35 to -15
Yield (%)	79	-	-

4. Conclusion

Biodiesel was prepared from WCO by three-step method, in three-step method aqueous sodium hydroxide solution was used for saponification. The optimum molar ratio for saponification by aqueous sodium hydroxide was 1:2 oil to NaOH and reaction time was 2.0h at 100°C. In acidification the molar ratio of soap to hydrochloric acid was 1:2 for sodium soap. In Esterification the optimum molar ratio of methanol to FFA was 6:1, the catalyst (HCl) concentration is 5wt% of FFA, the reaction temperature was 60°C and the reaction time was 2 hour, with silica gel reaction time was reduced to 80 min and FFA content was reduced to 0.94%. A factorial design was applied to find the optimum conditions for esterification reaction. At optimum conditions 99.06% conversion of the FFA to FAME was obtained and the viscosity, yield were 3.29mm^2/s and 79% wt/wt. The properties of produced biodiesel such as viscosity, specific gravity, cloud point, pour point, flash point etc. 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.

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