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Preparation and Optimization of Biodiesel Production from Mixed Feedstock Oil

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Abstract In this paper, production of biodiesel from mixed feedstock oil (MFO) by three-step method and optimization of the process were studied by using regressive analysis. The random mixer of different oil was used for biodiesel preparation. The MFO contains 12 wt% free fatty acid (FFA) and its viscosity was 67.5 mm^2/s. Because of higher FFA content transesterification method can't be applied, so three-step method was conducted for biodiesel preparation. 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. In the saponification reaction, various reaction parameters such as oil to sodium hydroxide molar ratio and reaction time were optimized. Produced sodium soap was acidified with excess molar ratio of HCl to produced FFA. In the esterification reaction, produced FFA was reacted with methanol in presence of acid catalyst and the FFA content was reduced to 0.98wt%. A factorial design was studied based on viscosity for esterification reaction and developed to obtain the higher yield of biodiesel. Finally various properties of biodiesel such as FFA content, viscosity, specific gravity, cetane index, pour point etc. were measured and compared with biodiesel and petro-diesel standard.

Keywords: *mixed feedstock, FFA, esterification, factorial design, biodiesel*

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1. Introduction

Presently the world's energy needs are met through non-renewable resources such as petrochemicals, natural gas and coal. Since the demand and cost of petroleum based fuel is growing rapidly, and if the present pattern of consumption continues, these resources will be depleted in few years. Hence, efforts are being made to explore for alternative source of energy. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available [1].

Energy consumption in developed countries has been increasing continuously over the past decades and is set to continue in the future. One possible alternative to fossil fuels is the use of fuels of plant origin [2]. Such fuels allow for a balance to be sought between agriculture, economic development, and the environment. Their undoubted advantages include maintaining cultivation croplands that otherwise would be abandoned, potentially developing new industrial activates, reducing dependence on oil. There is increasing interest in developing alternative energy resources. An immediately applicable option is replacement of diesel fuel by biodiesel, which consists of the simple alkyl esters of fatty acids. Without modification, diesel engine vehicles can use biodiesel fuels [3,4].

Biodiesel, defined as monoalkyl fatty acid ester (preferentially methyl and ethyl esters), presents a promising alternative fuel for use in compression-ignition (diesel) engines [5]. Fatty acids esters are formed by transesterification, also called alcoholysis, of vegetable oils. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance [6]. It has been proven that biodiesel fuels have viscosities close to those of diesel. In addition, although the volumetric heating values are a little lower, they have high cetane numbers and flash points [6]. Biodiesel is a strong candidate to replace petroleum diesel, as their characteristics are generally similar in addition to the many attractive advantages of biodiesel over petroleum diesel. These advantages include the following: it is plant oil rather than petroleum-derived and as such it is less toxic and comes from renewable sources; it is biodegradable; and relative to conventional diesel, its combustion products have reduced levels of particulates, carbon oxides, sulfur oxides, and under some conditions, nitrogen oxides [6,7].

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 Bakul oil, Pitraj oil, Karanja oil, Waste cook oil, Nahor oil, Seasame oil, castor oil etc. [8].

To reduce the burden on edible oils for biodiesel production we can use MFO sources. Different MFO sources are used for biodiesel production like rubber seed oil [9], used frying oil [10], castor oil [11], rapeseed oil, soybean soap stock, koroch seed oil, Karanja (Pongamia pinnata), Jatropha (Jatropha Curcas) [12], Neem (Azadirachta indica), Mahua (Madhuca indica),Simarouba (Simarouba indica), Jojoba (Simmondsia chinensis Link Schneider) [13,14]. Recently the planning commission of India has recommended Karanja and Jatropha oil for biodiesel production in India [15].

There are different methods for biodiesel preparation like base or acid catalyzed transesterification [16,17], two step method [18] and three-step method [9]. Encinar et. al. [10] prepared biodiesel from waste cook oil 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. [19] produced biodiesel from waste cook oil 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 non-edible mixed oil by three-step method to increase the reaction yield and minimize the methanol molar ratio. Additionally optimization study was done by the application of regression analysis 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. Collection of Oil

MFO was prepared by random mixing of Bakul oil, Waste cook oil, Nahor oil, Pitraj oil, Karanja oil and Castor oil. The oil composition was 33% WCO, 25% pitraj oil, 25% castor oil, 7% bakul oil, 5% nahor oil, 5% karanja oil. Oils were collected from the local sources of Sylhet city in Bangladesh. Finally the MFO was filtered and its properties were measured.

2.3. Preparation of Biodiesel by Three-Step Method

Three-step method consist of Saponification followed by acidification to produce FFA and finally esterification of FFA to produce biodiesel.

2.3.1. Saponification

For saponification process required amount of MFO was taken in a three necked flask and mixed with different stoichiometric amount of aqueous sodium hydroxide (NaOH) 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 mixture. Aqueous sodium hydroxide solution was prepared by dissolving required amount sodium hydroxide pellets in 60-90 mL 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 content was 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 titrimetric 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 MFO various physico-chemical properties were measured and compared with the standard biodiesel. The yield of biodiesel was calculated by the following equation:

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

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. [20].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 [20]. 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:

$$IV = \frac{(V_1 - V_2) \times S \times 0.1269 \times 100}{W} \quad (2)$$

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 MFO

The properties of MFO 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 MFO

FFA was prepared from MFO 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 present in Figure 1. From the Figure 1 it can be seen that, the optimum molar ratio of oil to NaOH was 1:2 and reaction time was 2.0 h.

Table 1. properties of MFO

Properties	Experimental Value
Color	Deep Brown
Specific gravity, at 25 °C	0.95
Kinematic viscosity (mm^2/s), at 40 °C	67.5
FFA content (%)	12.0
Moisture content (%)	0.35
Saponification value(mg KOH/gm of oil)	225
Cloud point (°C)	12
Pour point (°C)	6

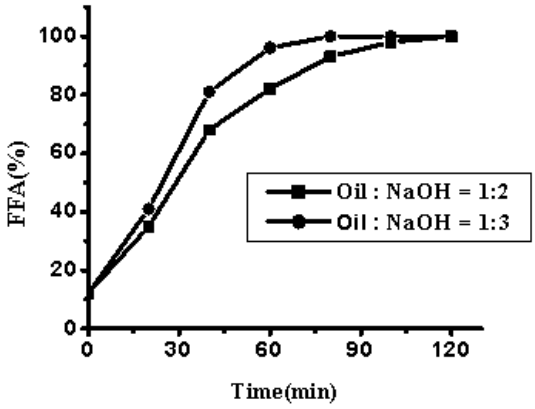

Figure 1. Preparation of FFA from MFO through saponification and acidification

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 used as a catalyst in Esterification reaction. 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 (HCl) concentration of 5 wt% of FFA. Further increasing the catalyst concentration conversion does not increase. The optimum catalyst concentration was 5 wt% of FFA.

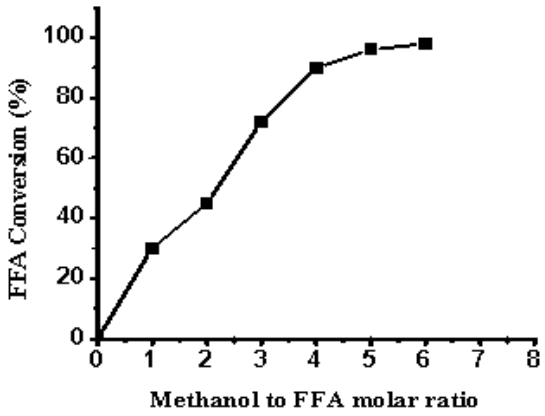

Figure 2. Effect of Methanol to FFA molar ratio on FFA conversion

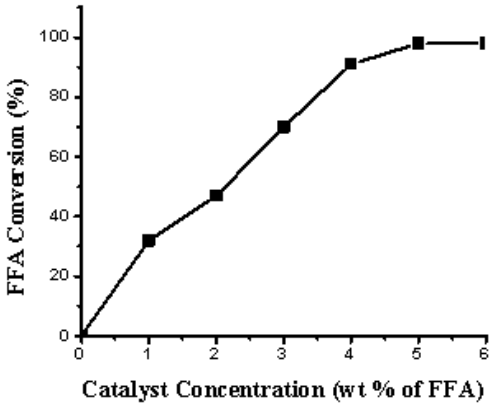

Figure 3. Effect of catalyst (HCl) concentration on esterification reaction

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 7.5 gm silica gel for 50 g 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 98% conversion was achieved within 90 minutes and reaction rate was increased.

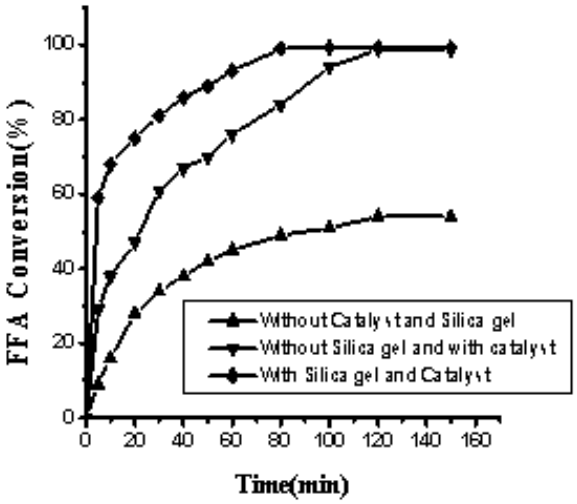

Figure 4. Effect of silica gel in esterification reaction

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 FFA conversion does not increase. The optimum temperature was 60 °C.

3.4. Optimization Study

Four factors (methanol to FFA molar ratio, catalyst concentration, temperature and reaction time) affect the biodiesel production process from MFO. 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.

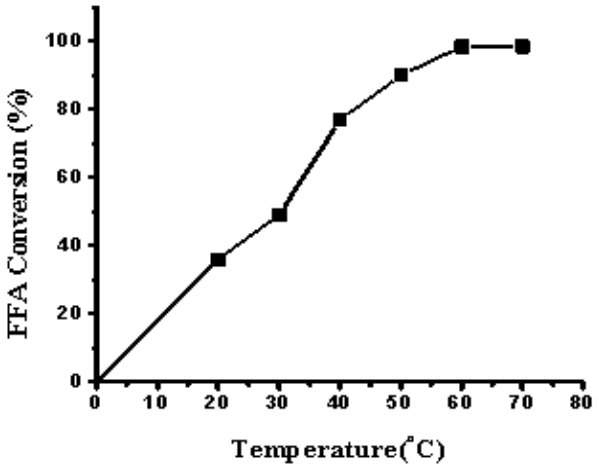

Figure 5. Effect of Temperature on esterification reaction

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	4.16	4.59	4.33	5.8	5.13	4.802	0.44
2	+1	+1	+1	-1	-1	14.25	12.36	13.1	14.23	13.63	13.514	0.64
3	+1	+1	-1	+1	-1	13.39	12.25	12.67	14.35	14.72	13.476	1.11
4	+1	+1	-1	-1	+1	13.63	10.51	10.23	9.94	11.26	11.114	2.21
5	+1	-1	+1	+1	-1	20.22	19.42	22.19	22.05	19.88	20.752	1.64
6	+1	-1	+1	-1	+1	11.35	10.91	12.06	13.12	11.43	11.774	0.73
7	+1	-1	-1	+1	+1	8.58	8.92	9.23	7.71	7.98	8.484	0.40
8	+1	-1	-1	-1	-1	22.34	21.52	20.9	20.61	23.68	21.81	1.53
											$\sum \overline{Y} = 105.72$	$\sum S_i^2 = 8.74$

Where Y is the viscosity of biodiesel and $\overline{Y}$ is average value of Y. The sample variances where 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 1.09.

Table 4. Sample Variances

S_1^2	0.44	S_5^2	1.64
S_2^2	0.64	S_6^2	0.73
S_3^2	1.11	S_7^2	0.40
S_4^2	2.21	S_8^2	1.53

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

$$\hat{Y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_{12} + b_{13}X_{13} + b_{23}X_{23} \quad (3)$$

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

$$\hat{Y} = 13.21 - 2.49X_1 - 1.34X_3 - 4.17X_4 - 1.07X_{12} + 1.41X_{23} \quad (4)$$

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 7.6,

where the experimental value was 5.82. 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 82%.

Table 5. Properties of biodiesel produced from MFO and comparison with standard biodiesel and diesel values

Properties	Produced biodiesel value	Biodiesel Standard [9,21]	Diesel standard [21]
Specific gravity, at 25 °C	0.82	0.88 (at 15.5^0 C)	0.85(at 15.5°C)
Kinematic viscosity (mm^2/s), at 40°C	3.96	1.9-6.0	1.3-4.1
Free fatty acid content (%FFA)	0.98	-	-
Moisture content (%)	0.05	0.05% max.	0.161
Saponification value	165	-	-
Flash point (°C)	155	100 to 170	60 to 80
Iodine value	82	-	-
Cloud point (°C)	3	-3 to 12	-15 to 5
Pour point (°C)	0	-15 to 10	-35 to -15

4. Conclusion

Biodiesel was prepared from MFO 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 2.0 h at 100 °C. In acidification the molar ratio of soap to hydrochloric acid was 1:1.5 for sodium 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 °C and the reaction time was 2 hour, with silica gel reaction time was reduced to 80 min and FFA content was reduced to 0.98 %. 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 etc. are nearest to the petro-diesel. The present experimental results support that produced biodiesel from MFO by this method can be successfully used as diesel.

References

[1] Srivastava, A. and Prasad, R., "Triglycerides-based diesel fuels," *Renewable and Sustainable Energy Review*, 4 (2), 111-133, 2000.

[2] Shay, E.G., "Diesel fuel from vegetable oils: status and opportunities," *Biomass & Bioenergy*, 4, 227-242, 1993.

[3] Knothe, G., Gerpen, J.V. and Krahl, J., "The Biodiesel Handbook," AOCS Press, Champaign, IL, USA, 2005, 36-44.

[4] Barnard,, T. M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M., and Wilhite, B.A., "Continuous-flow preparation of biodiesel using microwave heating," *Energy & Fuels*, 21, 1777-1781, Feb. 2007.

[5] Soumanou, M.M. and Bornscheuer, U.T., "Improvement in lipase-catalyzed synthesis of fatty acid methyl esters from sunflower oil", *Enzyme Microbial Technology*, 33, 97-103, 2003.

[6] Fukuda, H., Kondo, A. and Noda, H., "Biodiesel fuel production by transesterification of oils," *Journal of Bioscience and Bioengineering*, *92*(5), 405-416, Sep. 2001.

[7] Yousef, T., Al-Zuhair, S. and Al-Atabi, M., "Performance of diesel engine using an emulsion of biodiesel-conventional diesel fuel," *Journal of Mechanical Engineering*, 56 (3), 137-142, 2005.

[8] http://www.eoearth.org/article, 2010/04/05.

[9] Morshed, Mahbub, Ferdous, Kaniz, Khan, Maksudur R, Mazumder, M.S.I, Islam, M.A. and Uddin, Md.T., "Rubber seed oil as a potential source for biodiesel production in Bangladesh," *Fuel*, 90, 2981-2986, Jun.2011.

[10] Encinar, J.M., Gonzalez, J.F. and Rodrıguez-Reinares, Antonio, "Biodiesel from Used Frying Oil.Variables Affecting the Yields and Characteristics of the Biodiesel," *Industrial & Engineering Chemistry Research*, 44, 5491-5499, 2005.

[11] Plentz, Meneghetti, M., Simoni, Mario R., Meneghetti, R, Carlos. Wolf, Eid C. Silva, Gilvan E. S. Lima, Laelson de Lira Silva, Tatiana M. Serra, Fernanda Cauduro and Lenise, G. de Oliveira, "Biodiesel from Castor Oil: A Comparison of Ethanolysis versus Methanolysis," *Energy & Fuels*, 20, 2262-2265, Jun. 2006.

[12] Houfang, Lu, Yingying, Liu, Hui Zhou, Ying Yang, Chen, Mingyan and Bin, Liang, "Production of biodiesel from *Jatropha curcas* L. oil," *Computers and Chemical Engineering*, 33, 1091-1096, 2009.

[13] Wang, Yong, Wang, Xingguo, Liu, Yuanfa, Ou, Shiyi, Tan, Yanlai and Tang, Shuze, "Refining of biodiesel by ceramic membrane separation," *Fuel Processing Technology*, 90, 422-427, Jan.2009.

[14] Sharma, Y.C., Sing, B. and Upadhyay, S.N., "Advancements in development and characterization of biodiesel: A review," *Fuel*, 87, 2355-2373, Feb.2008.

[15] Murugesan, A., Umarani, C., Chinnusamy, T.R., Krishnan, M., Subramanian, R. and Neduzchezhain, N., "Production and analysis of bio-diesel from non-edible oils – a review," *Renewable and Sustainable Energy Review*, 13, 825-834, Jan.2009.

[16] Meher, L.C., Sagar,Vidya D.Nnik, S.N., "Technical aspects of biodiesel production by transesterification - a review," *Renewable and sustainable Energy Review*, 10, 248-268, 2006.

[17] De, B.K. and Bhattacharyya , Biodiesel from minor vegetable oils like karanja oil and nahor oil, *Wiley-VCH Verlag GmbH, D-69451 Weinheim*, 1999, 404-406.

[18] Zullaikah, Siti, Lai, Chao-Chin, Vali, Shaik, Ramjan and Ju, Yi-Hsu, "A two-step acid-catalyzed process for the production of biodiesel from rice bran oil," *Bioresource Technology*, 96, 1889-1896, 2005.

[19] Zheng, S., Kates, M., Dube, M.A. and McLean, D.D., "Acid-catalyzed production of biodiesel from waste frying oil," *Biomass & Bioenergy*, 30, 267-272, Jan.2006.

[20] Jeffery, G.H, Bassett, J, Mendham, J. and Denney, R.C., "Vogel's textbook of quantitative chemical analysis," 5th edition, *Longman Scientific and Technical, UK*, 1991, 308-309.

[21] Joshi, R.M. and Pegg, M.J. "Flow properties of biodiesel fuel blends at low temperatures," *Fuel*, 86, 143-151, 2007.