www.ioirp.com
International Journal of Innovative Research in Technology, Science & Engineering (IJIRTSE)
ISSN: 2395-5619, Volume – 1, Issue – 10. December 2015

Studies on Optimization of Biodiesel Production-Snail Shell as Eco-Friendly Catalyst by Transesterification of Neem oil

Dr.S.K.Mohan
Department of Chemical Engineering
The Kavery College of Engineering
Salem, Tamilnadu, India
skmohan75@gmail.com

***Abstract*— Biodiesel is a promising alternative fuel that can be derived from waste oil, animal fat or vegetable oil that has been converted into methyl esters through transesterification with alcohol. In the present research work, biodiesel was produced from neem oil using calcium oxide from snail shell as a heterogeneous catalyst. Central Composite Design of Response Surface Methodology (RSM) was used to optimize the biodiesel production parameters. A quadratic polynomial equation was obtained for biodiesel yield by multiple regression analysis. Interactions between the variables were validated statistically. The optimum process parameters for biodiesel production are reaction time of 3h, reaction temperature of 65°C, amount of catalyst of 10 % (wt) and methanol to oil molar ratio of 9:1 respectively. The optimum yield of biodiesel was found to be 96%.**

Keywords*— *Biodiesel; Transesterification; Neem oil; Snail shell; Response Surface Methodology

I. Introduction

The increasing awareness of the depletion of fossil fuel resources and the environmental benefits of biodiesel fuel has made it more attractive in recent times. Its primary advantages deal with it being domestically produced, renewable fuel that can be manufactured from vegetable oils, animal fats, or recycled restaurant grease for use in diesel vehicles. Biodiesel's physical properties are similar to those of petroleum diesel, but it is a cleaner-burning alternative. Using biodiesel in place of petroleum diesel, especially in older vehicles, can reduce emissions [1]. Biodiesel is prepared from various sources of edible oil such as soybean, cotton seed, sunflower, rapeseed, palm, canola etc. throughout the world [2]. Heterogeneous solid base catalyst such as calcium oxide has some advantages over homogeneous catalyst because the catalyst can be reused and is inexpensive. Generally Calcium oxide has a tolerance of moisture and free fatty acids and noncorrosive. Recently Calcium oxide derived from natural resources such as chicken egg shell [3], fish bone waste [10], mollusk shells [7], oyster shell [9] and mussel shell [8] has been used as a heterogeneous catalyst for biodiesel production. Response Surface Methodology (RSM) is a collection of mathematical and statistical technique, which provides important information regarding the optimum level of each variable along with its interactions with other variables and their effects on product yield. It reduces the number of experiments without neglecting the interactions among the parameters. This multivariate approach also improves statistical interpretation possibilities and evaluates the relative significance of several contributing factors even in the presence of complex interactions [4,6].

In the present work, optimization of biodiesel production by transesterification of neem oil using calcium oxide as a catalyst from snail shell was carried out using a sequential strategy of the experimental design. The effect of process parameters namely reaction time, reaction temperature, catalyst size and methanol to oil molar ratio were investigated.

II. Materials and Methods

A. Materials

Neem oil was purchased from local market and chemicals used in the experiments were purchased from Hi-Media, Mumbai and were of the highest purity. The snail shell was collected from garden and it was rinsed with running water to remove dust and impurities and then dried in an oven.

B. Preparation of snail shell as catalyst

CaO catalyst was prepared from snail shell by calcination method. The snail shell was cleaned thoroughly with running water for removal of organic matter and dried for whole night at 120°C and then the snail shell (100-200 mesh) was calcined at 850°C in air atmosphere with a heating rate of 10°C/min for 4 h. All calcined samples were kept in the closed vessel to avoid the reaction with humidity in air and carbon dioxide before used. Because the CaO catalyst will be reacted with CO_2 and converted into $CaCO_3$, thus reducing its activity as a catalyst.

C. Methods

Transesterification reactions were carried out in 500 ml of 3 necked round bottom flask. The reactor was filled with 100 ml of refined neem oil. Sodium hydroxide catalyst was dissolved in methanol and then added to the reactor. The mixture was heated to selected temperature. After the end of the reaction, the mixture was cooled to room temperature and transferred to a separating funnel. The two layers (biodiesel and glycerol) were separated by sedimentation. The methyl ester phase (biodiesel) was washed with hot distilled water and drying was done by heating the biodiesel to a temperature above 100°C to remove water molecules. Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. Alcohol combines with the triglycerides to form glycerol and esters. A catalyst is usually used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Alkali-catalyzed transesterification much faster than acid-catalyzed transesterification and is most often used commercially (Boey et al., 2009). The transesterification process parameters such as reaction time, reaction temperature, amount of catalyst and methanol to oil molar ratio were varied to attain maximum biodiesel conversion. By inserting methanol and oil into a flask with a variable ratio of 7:1, 8:1, 9:1,10:1 and 11:1 and adding calcium oxide catalyst as many as 6,8,10,12 and 14% (wt). After a homogeneous mixture, neem oil is inserted into a flask and heated at a variable temperature of 55ºC, 60ºC, 65ºC, 70ºC and 75ºC at 1h, 2h, 3h, 4h and 5 h. After the reaction is completed, the catalyst was screened by using a whatmann filter paper and the transesterification products were allowed to settle overnight for the clear separation of biodiesel and glycerol.

III. RESULTS AND DISCUSSION

A. Optimization of process parameters for production of biodiesel by neem oil with snail shell as catalyst using RSM

The Response Surface Methodology used in the present study is a central composite design involving four different factors. The dependent variables selected for this study is biodiesel conversion. The independent variables chosen are reaction time (X_1), reaction temperature (X_2), catalyst size (X_3) and molar ratio(X_4). Experiments are conducted in a randomized fashion. Table 1 shows the coded level and actual level of the independent variables employed in the design matrix. The experimental design matrix with five different reaction time namely 1h, 2h, 3h, 4h and 5 h; five different reaction temperature namely 55ºC, 60ºC, 65ºC, 70ºC and 75ºC; five different amount of catalyst 6, 8, 10, 12 and 14% by wt of oil and molar ratio 7, 8, 9, 10 and 11 are employed for neem oil to cover the spectrum of combinations of independent variables in CCD. The CCD contains a total of thirty one experimental trials involving the replications of seven central points as given in Table 2 to study the linear, squared and interactive effects of the four independent variables on biodiesel production by neem oil for transesterification with snail shell as catalyst using RSM. Design-Expert (version 7.0) software was used for experimental design.

TABLE I CODED LEVEL AND ACTUAL LEVEL OF THE INDEPENDENT VARIABLES FOR THE DESIGN OF EXPERIMENT FOR BIODIESEL CONVERSION USING NEEM OIL

Independent Variables	**Symbols**	**Coded levels**				
		-2	-1	0	+1	+2
Reaction time (h)	X_1	01	02	03	04	05
Reaction temperature (°C)	X_2	55	60	65	70	75
Amount of Catalyst (%)	X_3	06	08	10	12	14
Molar ratio	X_4	07	08	09	10	11

The second order polynomial model describing the effect of the variables on biodiesel production is given by “(1)”.

$$Y = 121.27 + 0.812 X_1 + 1.413 X_2 + 2.012 X_3 + 0.992 X_4 - 8.329 X_1^2 - 13.251 X_2^2 - 13.141 X_3^2 - 13.119 X_4^2 - 0.263 X_1X_2 - 2.618 X_1 X_3 + 0.238 X_1 X_4 - 0.514 X_2X_3 - 3.251 X_2X_4 - 0.601 X_3 X_4 \quad (1)$$

Where Y is the biodiesel conversion (%) as a function of the coded levels of reaction time (X_1), reaction temperature (X_2), Amount of catalyst (X_3) and molar ratio(X_4).

www.ioirp.com

International Journal of Innovative Research in Technology, Science & Engineering (IJIRTSE)
ISSN: 2395-5619, Volume – 1, Issue – 10. December 2015

Based on the experimental response, the biodiesel conversion by snail shell using neem oil varies from 70% to 96%. The Analysis of variance (ANOVA) demonstrates that the model is highly significant as $p < 0.001$. The ANOVA for the response surface is shown in Table 3. ANOVA of the regression model demonstrated that the model is significant for biodiesel conversion. Values of "Prob>F" less than 0.05 indicate the model terms are significant. Values greater than 0.1 indicate the model terms are not significant. In the present work, the squared effect of reaction time, reaction temperature, catalyst size and molar ratio are found to be significant for maximum biodiesel production. The coefficient of determination (R^2) for the biodiesel production is calculated as 0.9251, which is close to 1 and can account for up to 92.51% of the variability of the response.

TABLE- 2 FIVE LEVEL CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD) AND THE EXPERIMENTAL RESPONSES OF DEPENDENT VARIABLE OF BIODIESEL CONVERSION

Run No.	X_1	X_2	X_3	X4	Biodiesel conversion	
					Experimental	RSM Predicted
1	0	0	0	0	84	83
2	0	0	0	0	88	86
3	1	1	1	1	85	85
4	1	-1	1	-1	82	80
5	1	-1	1	1	81	82
6	-1	1	-1	1	80	79
7	-1	1	-1	-1	86	86
8	-1	-1	-1	-1	91	87
9	0	2	0	0	95	94
10	1	-1	-1	-1	94	94
11	0	0	0	0	89	86
12	0	0	0	0	79	75
13	1	-1	-1	1	94	94
14	-1	-1	1	1	96	94
15	0	-2	0	0	86	86
16	0	0	0	0	86	84
17	0	0	0	0	80	79
18	1	1	1	-1	80	80
19	0	0	0	2	93	94
20	-1	-1	1	-1	83	82
21	0	0	0	-2	81	78
22	0	0	2	0	82	79
23	-2	0	0	0	76	76
24	0	0	-2	0	73	76
25	-1	1	1	1	94	95
26	-1	-1	-1	1	94	96
27	1	1	-1	1	78	80
28	1	1	-1	-1	86	82
29	-1	1	1	-1	83	86
30	0	0	0	0	81	80
31	2	0	0	0	70	73

TABLE 3 ANALYSIS OF VARIANCE (ANOVA) FOR THE QUADRATIC POLYNOMIAL MODEL FOR BIODIESEL PRODUCTION USING NEEM OIL

Source	Sum of Squares	Degrees of freedom (DF)	Mean square (MS)	*F*-value	P >F
Regression	1353.5	14	966.61	14.11	< 0.0001
Linear	198.0	4	49.50	0.72	0.5892
Square	1314.4	4	3278.60	47.85	< 0.0001
Interaction	220.1	6	36.69	0.54	0.7741
Residual Error	106.4	16	68.52	-	-
Lack-of-Fit	106.4	10	109.43	322.77	0.000
Pure Error	0.000	6	0.00	-	-
Total	1460	30			

The interaction effects of variables on biodiesel production are studied by plotting the three dimensional response surfaces with the vertical axis representing biodiesel conversion (response) and two horizontal axes representing the coded levels of two independent variables, while keeping other variables at their central level (0). The results are shown in Fig 1 to Fig 6.

The optimum values of the process parameters for biodiesel production are reaction time of 3 h, reaction temperature of 65°C, catalyst concentration of 10 (% wt of oil) and methanol to oil molar ratio of 9:1 respectively. The obtained optimum parameters in this study are in reasonable agreement with several research works (Sulaiman et al., 2015, Putri et al., 2012). Therefore, the present research study shows that base CaO heterogeneous catalyst is a potential catalyst for the production of biodiesel from neem oil via heterogeneous transesterification. The optimization result also tells the same result as the ANOVA output. The ANOVA output shows that the transesterification process is highly and significantly affected by the temperature, catalyst concentration and the interaction between the temperature and the catalyst.

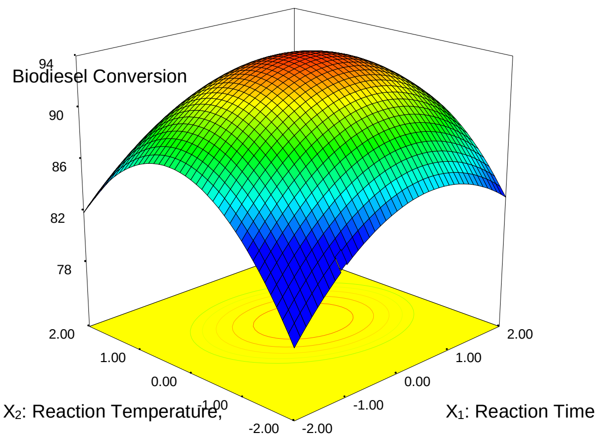

Fig 1. Response Surface plot showing the effect of reaction temperature and reaction time on biodiesel conversion

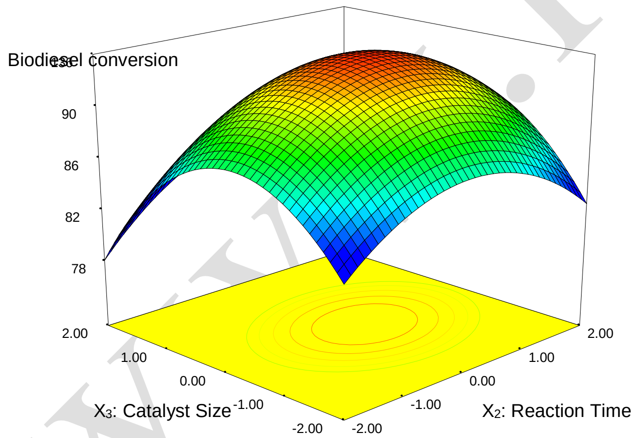

Fig 2. Response Surface plot showing the effect of amount of catalyst and reaction time on biodiesel conversion

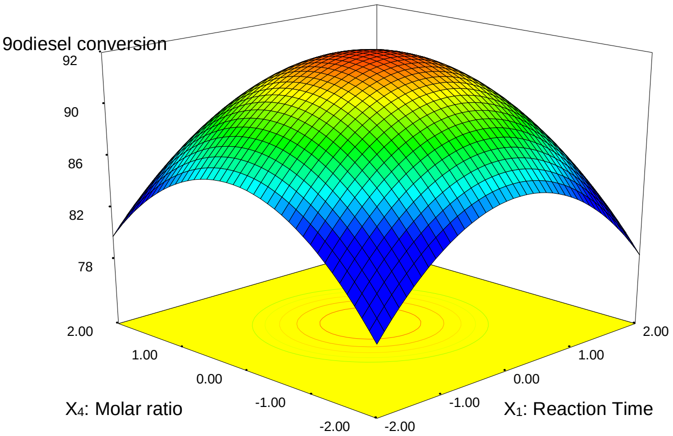

Fig 3. Response Surface plot showing the effect of molar ratio of methanol to oil and reaction time on biodiesel Conversion

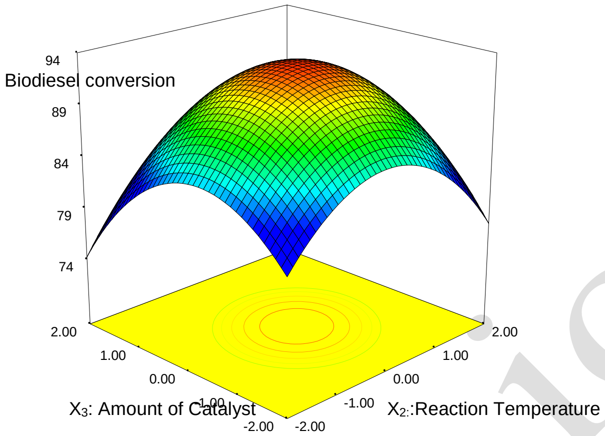

Fig 4. Response Surface plot showing the effect of amount of catalyst and reaction temperature on biodiesel conversion.

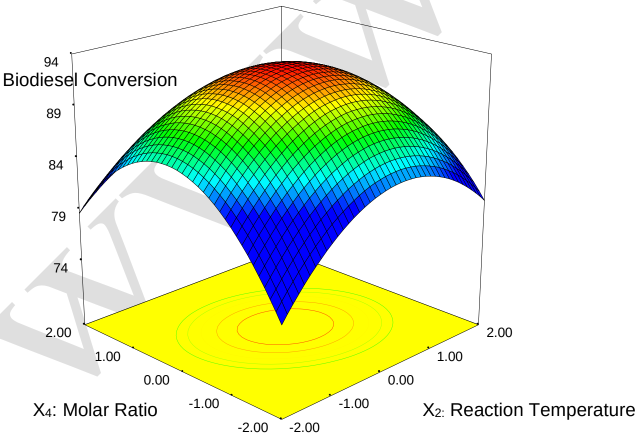

Fig 5. Response Surface plot showing the effect of molar ratio of methanol to oil and reaction temperature on biodiesel conversion

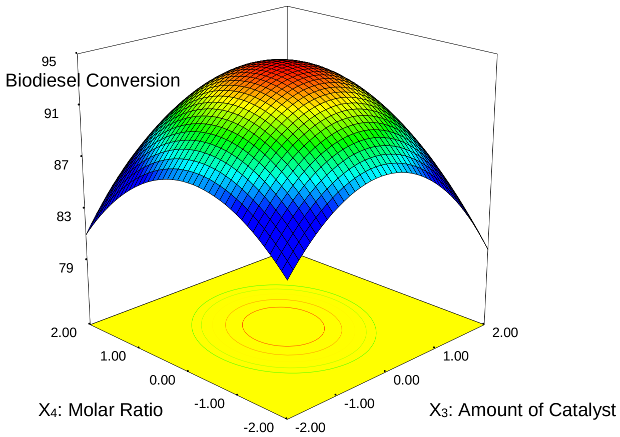

Fig 6. Response Surface plot showing the effect of molar ratio of methanol to oil and amount of catalyst on biodiesel conversion

IV. CONCLUSIONS

The snail shells are used as the catalyst for the production of biodiesel process. This snail shells contains calcium carbonate which is converted to calcium oxide after the calcination process at a temperature of 850°C for 4 h and calcium oxide was acknowledged as an effective heterogeneous catalyst for the transesterification of neem oil and methanol. This study has demonstrated the feasibility of using calcium oxide as catalyst to produce biodiesel from waste cooking oil via a one alkali catalyst technique. The response surface technique was used to determine the optimal condition that can be used to produce biodiesel from neem oil. The optimum process parameters for biodiesel production are reaction time of 3h, reaction temperature of 65°C, catalyst concentration of 10 (% wt of oil) and methanol to oil molar ratio of 9:1 respectively. The optimum yield of biodiesel was found to be 96%. The results prove that the calcium oxide catalyst from snail shell had excellent activity during transesterification reaction.

Acknowledgment

The authors express their sincere thanks to the Management of The Kavery Group of Institutions and Principal, The Kavery College of Engineering for providing the necessary facilities for the successful completion of this research work.

References

[1] G. Vincente, M. Martinez, J. Aracil," Integrated biodiesel production: a comparison of different homogeneous catalysts systems," Bioresour. Technol, 92, 297–305, 2004.
[2] X. Lang, A.K Dalai, N.N Bakhshi, M.J. Reaney, P.B. Hertz, "Preparation and characterization of bio-diesels from various bio-oils," Bioresour. Technol, 80, 53–62, 2001.
[3] K. Chojnacka, " Biosorption of Cr(III) ions by eggshells," J.Hazard. Mater. 121, 167–173, 2005.
[4] K. Jatinder, B.S. Chadha and H.S. Saini, "Optimization of culture conditions for production of cellulases and xylanases by Scytalidium thermophilum using Response Surface Methodology," World J Microb Biot, 22: 169–176, 2006.
[5] PL. Boey, GP. Maniam, and SA. Hamid, "Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) shell as a heterogeneous catalyst," Bioresour. Technol, 100 (24), 6362–6368, 2009.
[6] SK. Mohan, T. Viruthagiri and C. Arunkumar, "Enhanced Production of Tannase from Redgram Husk using Response Surface Methodology," Inter. Journal of Pharma Sci. and Research, 4(12), 144-153, 2013.
[7] N. Viriya-empikul, P. Krasae, W. Nualpaeng, B. Yoosuk, K. Faungnawakij, "Biodiesel production over Ca-based solid catalysts derived from industrial wastes," Fuel, 92, 239–244, 2012.
[8] R. Rezaei, M. Mohadesi, GR. Moradi, "Optimization of biodiesel production using waste mussel shell catalyst," Fuel, 109, 534–541, 2013.
[9] N. Nakatani, H. Takamori, K. Takeda, H. Sakugawa, "Transesterification of soybean oil using combusted oyster shell waste as a catalyst," Bioresou. Technol, 100, 1510-1513, 2009.
[10] S. Sulaiman, Syakirah, N. Khairudin, P. Jamal, M.Z. Alam, "Fish Bone Waste as Catalyst for Biodiesel Production," J. Trop. Resour. Sustain. Sci. 3, 180-184, 2015.
[11] EMM Putri, M. Rachimoellah, N. Santoso and F. Pradana, "Biodiesel Production from Kapok Seed Oil (*Ceiba Pentandra*) through the Transesterification Process by using Cao as Catalyst, Global Journal of Researches in Engg. Chem. Engg., 12(2), 2012.