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Research Article

Optimization of Reaction Parameters by Response Surface Methodology

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Abstract

In this paper response surface methodology (RSM), has been used to study the effect of variables of biodiesel, the four variables of transesterification reaction methanol to oil molar ratio, catalyst (NaoH) concentration, reaction temperature and reaction time to viscosity of rice bran oil methyl esters. Central composite design with 2^4 full factorial experiments was conducted to develop the quadratic model. The empirical model predicted that gives lowest viscosity of biodiesel would be 4.32 Cst at the follow operating conditions; a reaction time 60 min, a reaction temperature 55^0C, a catalyst concentration 1.5 wt %, and methanol to oil ratio 6: 1.The quadratic model is suitable to maximize the viscosity of biodiesel. All the properties were determined for the same experiment and these are satisfying almost all specification.

Keywords: *RSM, Optimization of parameters etc.*

Introduction

As supply of fossil fuel is limited whilst energy demand continues to rise, hence alternative renewable fuels have received increasing attention for future utilization. In this respect, fermentation, transesterification and pyrolysis of biomass, industrial and domestic wastes have been proposed as alternative solutions for the increasing of energy demand and environmental awareness (Lima, Daniela G *et al*, 2004).

Among the renewable resources for the production of alternative fuels, triglycerides have attracted much attention as alternative diesel engine fuels (Shay, E.G, 1993). However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct injection and indirect type diesel engines because of their high viscosities and low volatilities, injector coking and trumpet formation on the injectors, higher level of carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil, acid composition (the reactivity of unsaturated hydrocarbon chains), and free fatty acid content (Ma, F., Hanna, 1999; Srivastava, 2000; Komers *et al*, 2001).

In transestrification reaction, the vegetable oil or animal fat is reacted in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the FA mixture that is found in the parent vegetable oil or animal fat (Gunstone *et al*, 2001).

Biodiesel esters are characterized by their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pore point, gross heat of combustion, and volatility. Biodiesel fuels produce slightly lower power and torque and consume more fuel than No. 2 diesel (D2) fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability (Bala *et al*, 2005).

Most of the western countries use soybean, sunflower, saffola, rapeseed, palm oil, etc. for production of biodiesel and investigations on engines (Korbitz W., 1999; Dorado MP*et al*, 2005; Bozbas K, 2005). These oils are edible in nature and developing countries like India cannot afford edible oils as a fuel substitute. Use of such edible oil to produce biodiesel in India is not feasible in view of a big gap in the demand and supply of such oils in the country for dietary consumption. Increased pressure to augment the production of edible oils has also put limitations on the use of these oils for production of biodiesel. To extend the use of biodiesel, the main concern is economic viability of producing biodiesel. The price of feedstock (vegetable oil) is one of the most significant factors, which consists of approximately 75–88% of the total biodiesel production cost (Dorado MP *et al*, 2005;

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Bozbas K., 2005; Hass MJ *et al*,2006). Obviously, developing nations have to focus their attention on oils of non-edible nature, which are cheaper. In India, a variety of non-edible oils like linseed, mahua, karanja, rice bran and jatropha are available in surplus quantities.

India is the second largest producer of rice in the world, next to China, with the potential to produce about 1 million tonnes of rice bran oil per annum. Rice bran is a low value co-product of rice milling, which contains approximately 15–23% oil. Currently, the industry is processing about 3.5 million tonnes of rice bran, leading to a production of about 0.65 million tonnes of oil, and an additional 0.33 million tonnes could be produced through modernizing the huller rice mills and installation of rice bran oil refineries (Shailendra Sinha *et al*, 2009).

The properties of biodiesel are similar to those of diesel fuels. Viscosity is the most important property of biodiesels since it affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets (Islam *et al*, 2004).

In this work, the production of methyl ester from rice bran oil was studied using alkali catalyst. The method was developed and optimized by following response surface methodology. A 2^4 full factorial central composite design based on response surface methodology (RSM) is used in this study. The method is powerful tool to estimate improved process yield, reduced variability and closer conformance to nominal or target requirement, reduce overall costs. In the present work this methodology has been applied to obtain the relationship between viscosities of methyl ester and the operating conditions; reaction temperature, reaction time, catalyst concentration and methanol to oil molar ratio affecting the alkali catalytic transesterification reaction and response surface methodology is used to evaluate the optimum values for the operating variables in order to obtain the minimum value of viscosity of biodiesel.

Methods

Material and Equipments

Rice bran oil was purchased from local market. According to lab testing rice bran oil was characterised by acid value 4.81, free fatty acid content is 2.84%, viscosity is 42.84 Cst, methanol and sodium hydroxide used having 99.8% purity by MEARK. A 250 ml three neck round bottom flask was used as batch reactor. The condenser assembly was fitted to a batch reactor at one side neck. The mechanical stirrer was arranged through the central neck of the flask and through another side neck thermometer is fixed to record the temperature. Batch reactor is fitted in constant temperature bath to maintain constant reaction temperature.

Experimental procedure

Initially the range for operating condition was taken according to physical properties and stichiometric ratio. Methanol having boiling point 62^{0}C, therefore higher level for reaction temperature was taken 60^{0}C. As per stichiometry reaction carried out at 3:1 methanol to oil molar ratio. The reaction is a reversible one, so, an excess of methanol is necessary to drive the equilibrium towards methyl ester formation. Hence actual experimental tests had taken at higher molar ratio.

For each experiment, rice bran oil of measured 100ml was added to a batch reactor and heated to specific temperature. Next, make dissolved solution of measured quantity of methanol and sodium hydroxide. By keeping required temperature constant add methanol, sodium hydroxide solution in batch reactor where stirrer having speed 500 ±10 rpm. The reaction time is varied in the range of 30 to 60 min.

Analysis

Viscosity is an important property of engine fuel and it determines the rate of atomization may lead to an increase in ignition retardation, incomplete combustion and ultimately power loss. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight that of the triglyceride and reduces the viscosity. Therefore decrease in viscosity shows the more conversion of triglyceride into methyl ester and which gives more biodiesel yield. Kinematic viscosity of sample was determined by measuring by the time of the flow of the fixed volume of liquid at a particular temperature through calibrated capillary of 'U' tube viscometer.

Statistical Analysis

A factorial design was performed to study the influence of the variable on the process and the interaction among variables. For the production of methyl ester by transesterification from rice bran oil using sodium hydroxide as a catalyst was developed and optimised following the response surface methodology. In this study experimental design applied was full 2^4 factorial design i. e. Four factors each at five levels. The response selected was the previously defined biodiesel viscosity.

A full factorial central composite factorial design is used to acquire data to fit an empirical quadratic model. For four factors the model taken the following form;

$$Y_i = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^{\,2} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j + e_i \quad (1)$$

Where Y_i is the process response variable. X_i, X_j, X_k, and

X_l are dependent variables; reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration respectively. And β_0 to β_i are regression coefficient.

In developing the regression equation, the test variables are coded according to the equation:

$$x_i = (X_i - X_i^*) / \Delta X_i \quad (2)$$

Where x_i is the coded value of the ith independent variable; X_i is the uncoded value of the ith independent variable; X_i^* is the uncoded value of the ith independent variable at the centre point and ΔX_i is the step change value[14].

Result and discussion

The design of experiment of dependent variables and response is present in Table 1. All 30 of the designed experiments were conducted, and the results were analyzed. In order to optimize the reaction condition of rice bran oil biodiesel, the central composite rotatable design, which is generally the best design for response surface optimization, was selected with five-level-four-factors.

The Analysis of variance (ANOVA) for the response surface second order model is given in Table 2. A p-value showed that all of the linear coefficients were more highly significant than their quadratic and cross product terms. However, in order to minimize error, all of the coefficients were considered in the design. According to the ANOVA analysis of factors, we noted a low lack of fit. This indicates that the model does indeed represent the actual relationships of reaction parameters, which are well within the selected ranges (Table 2).

Experimental results were fitted to a quadratic model and following equation were obtained.

$$Y = 120.187 + 0.27X_1 - 2.68X_2 - 5.27X_3 - 22.78 X_4 - 0.0024 X_1 X_2 + 0.0008 X_1 X_3 + 0.016X_2 X_3 + 0.061 X_1 X_4 - 0.079 X_2 X_4 - 0.198 X_3 X_4 + 0.0028 X_1^2 + 0.025 X_2^2 + 0.372 X_3^2 + 8.43 X_4^2$$

The model F-value of 37.665 implies that the model is significant. The p-value is less than 0.0001, i.e., there is a 0.01% chance that this error is caused by noise. This implies a very high significance of the regression model. The goodness of fit of the model is checked by the determination coefficient (R2). In this case, the value of R2 (= 0.9723) indicates that the model does not explain only 9.20% of the total variations. The value of adjusted determination coefficient (Adj R2 = 0.9465) is also high to get a high significance of the model. At the same time a relatively lower value of coefficient of variation (CV = 4.35%) indicates a better precision and reliability of experiments carried out[15]. In linear terms, reaction time, temperature and methanol to oil molar ratio, and in quadratic terms, squared catalyst concentration, temperature, methanol to oil molar ratio (*P*-value = <0.0001) and catalyst concentration, squared reaction time (*P*-value = 0.0005) made the most significant contributions to the fitted model. First order interaction effects of the four terms were statistically significant, with the greater significant for the interaction of reaction time x temperature (P = 0.0983), reaction time x catalyst concentration (P = 0.0427), temperature x methanol to oil molar ratio (P = 0.1015), temperature x catalyst concentration (P = 0.1711).

The graphical representation of the relationship between the responses and process parameters, are presented in fig. 1–6. The contour plots were made by taking an infinite number of combinations of the values of the two test variables at a time and keeping the values of the remaining two test variables constant. Contour plots are useful for understanding the interaction of two test variables and determining their optimum levels by holding other test variables constant. Figure 1 shows the effect of reaction time and reaction temperature on rice bran oil methyl esters viscosity. An increase in reaction temperature caused a decrease viscosity in methyl esters content. The reaction temperature also exerted a significant effect on the response. The response values reached the lowest level and most efficient near 55^{0}C and its interaction effect with reaction time, methanol to oil molar ratio, catalyst concentration is shown in fig 1, 3, 5 respectively.

The effects of reaction time and molar ratio on methyl ester viscosity are shown in Fig 4. The effect of reaction time is more significant than other variables because as time increases maximum reaction completed and minimum viscosity appears at 60 minute. The interaction effect of reaction time with temperature, catalyst concentration, and molar ratio is shown in fig. 1, 2 and 4 respectively.

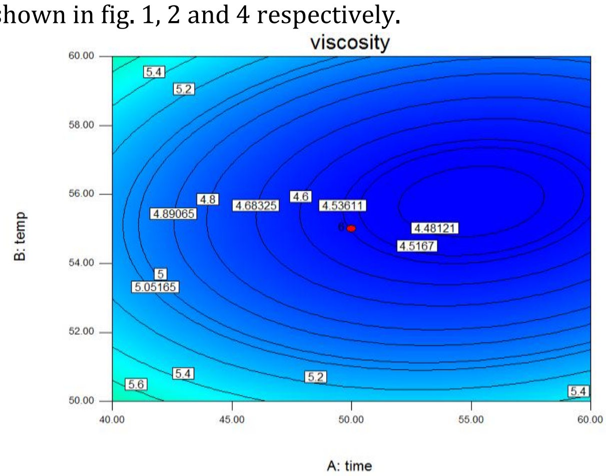

Fig.1 Contour plot of ester viscosity: effect of reaction temperature, time and their mutual interaction on ester viscosity. The value in prediction box indicates minimum ester viscosity while other variables are fixed

Table 1 Central composite design matrix of four variables in coded and actual units with observed responses

			Coded Variables			Uncoded Variables		
Exp. No.	**Reaction Time**	**Reaction Temp**	**Oil to Methanol Ratio**	**Cat. Conc.**	**Reaction Time**	**Reaction Temp**	**Oil to Methanol Ratio**	**Cat. Conc.**
					Min	**C**	**ml**	**wt%**
1	-1	-1	1	1	40	50	7.5	1.75
2	1	-1	1	1	60	50	7.5	1.75
3	-1	-1	-1	1	40	50	4.5	1.75
4	0	2	0	0	50	65	6	1.5
5	1	-1	-1	1	60	50	4.5	1.75
6	0	0	0	0	50	55	6	1.5
7	-1	-1	-1	-1	40	50	4.5	1.25
8	0	-2	0	0	50	45	6	1.5
9	0	0	0	-2	50	55	6	1
10	-2	0	0	0	30	55	6	1.5
11	0	0	0	0	50	55	6	1.5
12	0	0	0	2	50	55	6	2
13	1	1	1	1	60	60	7.5	1.75
14	0	0	0	0	50	55	6	1.5
15	0	0	-2	0	50	55	3	1.5
16	0	0	0	0	50	55	6	1.5
17	0	0	0	0	50	55	6	1.5
18	0	0	0	0	50	55	6	1.5
19	-1	-1	1	-1	40	50	7.5	1.25
20	1	1	-1	-1	60	60	4.5	1.25
21	1	-1	-1	-1	60	50	4.5	1.25
22	1	1	-1	1	60	60	4.5	1.75
23	-1	1	-1	-1	40	60	4.5	1.25
24	2	0	0	0	70	55	6	1.5
25	1	-1	1	-1	60	50	7.5	1.25
26	-1	1	-1	1	40	60	4.5	1.75
27	-1	1	1	-1	40	60	7.5	1.25
28	-1	1	1	1	40	60	7.5	1.75
29	1	1	1	-1	60	60	7.5	1.25
30	0	0	2	0	50	55	9	1.5

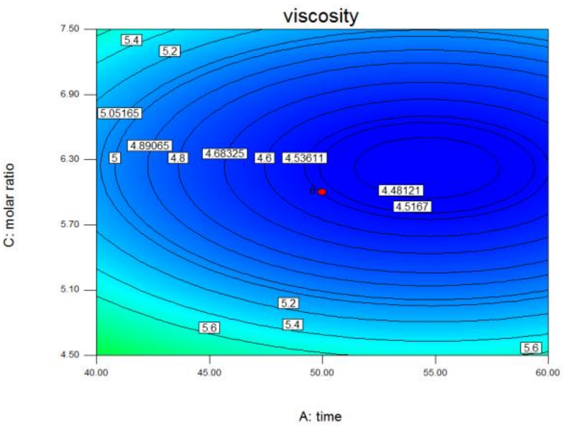

Fig.2 Contour plot of ester viscosity: effect of oil to methanol molar ratio, reaction time and their mutual interaction on ester viscosity. The value in prediction box indicates minimum ester viscosity while other variables are fixed.

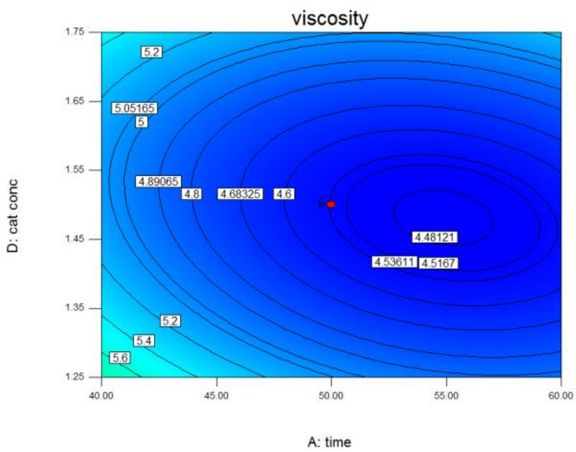

Fig.3 Contour plot of ester viscosity: effect of catalyst concentration, time and their mutual interaction on ester viscosity. The value in prediction box indicates minimum ester viscosity while other variables are fixed.

Table 2 Analysis of variance for Response Surface Quadratic Model

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	35.124	14	2.5089	31.4572	<0.0001	**significant**
A-time	1.722	1	1.7227	21.5997	0.0003	
B-temp	0.478	1	0.4789	6.0038	0.0270	
C-molar ratio	1.606	1	1.6068	20.1469	0.0004	
D-cat conc	0.0003	1	0.0003	0.0042	0.9490	
AB	0.237	1	0.2377	2.9798	0.1048	
AC	0.0027	1	0.0028	0.0346	0.8550	
AD	0.375	1	0.3752	4.7038	0.0466	
BC	0.232	1	0.2328	2.9189	0.1081	
BD	0.158	1	0.1580	1.9811	0.1797	
CD	0.0885	1	0.0885	1.1097	0.3088	
A^2	2.2589	1	2.2589	28.3230	<0.0001	
B^2	11.1289	1	11.1289	139.5371	<0.0001	
C^2	19.272	1	19.2721	241.6377	<0.0001	
D^2	7.6171	1	7.6171	95.5050	<0.0001	
Residual	1.1963	15	0.0798			
Lack of Fit	1.1946	10	0.1195	344.5986	<0.0001	
Pure Error	0.0017	5	0.0003			
Cor Total	36.3209	29				

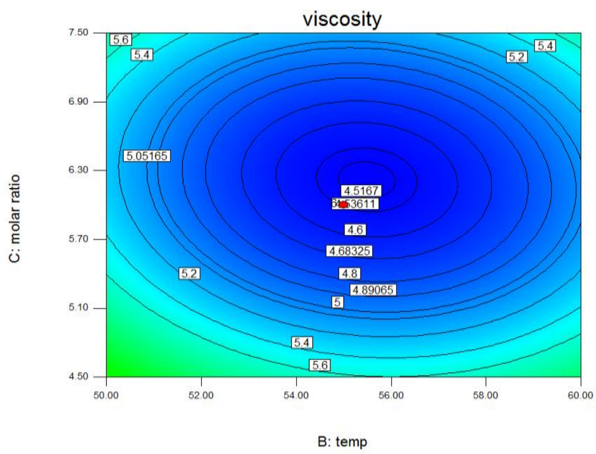

Fig.4 Contour plot of ester viscosity: effect of oil to methanol molar ratio, reaction temperature and their mutual interaction on ester viscosity. The value in prediction box indicates minimum ester viscosity while other variables are fixed.

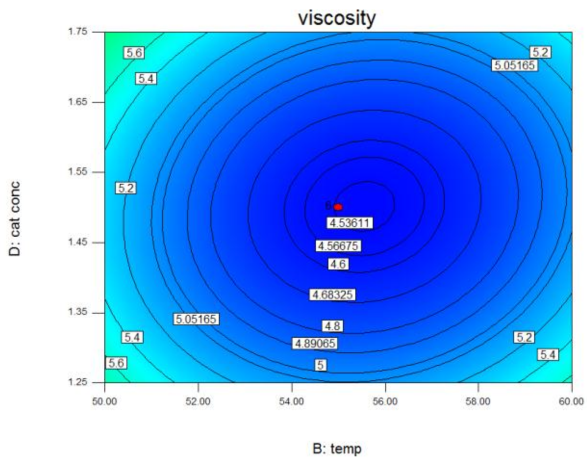

Fig.5 Contour plot of ester viscosity: effect of catalyst concentration, reaction temperature and their mutual interaction on ester viscosity. The value in prediction box indicates minimum ester viscosity while other variables are fixed.

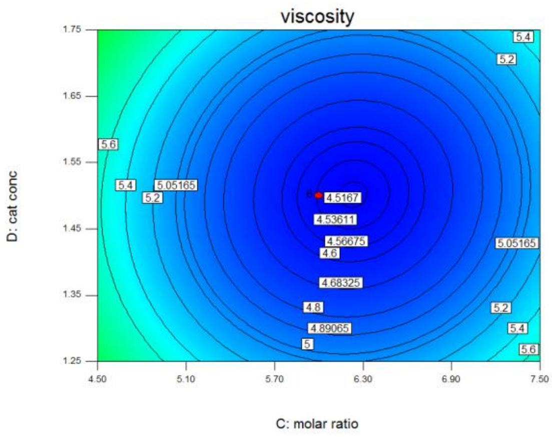

Fig.6 Contour plot of ester viscosity: effect of catalyst concentration, oil to methanol molar ratio and their mutual interaction on ester viscosity. The value in prediction box indicates minimum ester viscosity while other variables are fixed.

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