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OPTIMIZATION OF MICROWAVE-ASSISTED TRANSESTERIFICATION OF MAHUA OIL USING RESPONSE SURFACE METHODOLOGY

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Abstract- Biodiesel has recently become more attractive because of its environmental benefits and the fact that it is made from renewable resources and hence an attempt has been made to prepare bio diesel from Mahua Oil(MO) with a having high free fatty acid content. The objective of this work was to determine the relationship between various important parameters of the alkaline catalyzed transesterification process to obtain a high conversion to biodiesel. Response surface methodology (RSM) was used to analyze and to optimize the operating parameters of that process. A Box Behnken design was adopted to study the effects of the methanol to oil molar ratio, the catalyst concentration, reaction temperature, and reaction time on the conversion to biodiesel yield. Due to its high free fatty acid content, MO was processed in two steps. The first step acid esterification was carried out with the following conditions: 55 wt% of methanol to oil ratio, 1 ml of Sulfuric Acid, reaction temperature 60°C and time maintained is 4 minutes. The optimum conditions for the second step alkaline catalyzed transesterification of MO were found to be a methanol to oil molar ratio of 40 wt%, catalyst concentration of 1 wt%, reaction temperature of 53 °C and reaction time of 120 seconds. At the calculated optimum condition, the conversion to biodiesel yield reached to 95.54%. Under these same conditions, the experimental value was 96%.The result from the RSM analysis indicated that the methanol to oil molar ratio, catalyst concentration and reaction time had the most significant effects on the conversion to biodiesel.

KEYWORDS: Biodiesel, Free Fatty Acid Content, Mahua oil, Microwave, Response Surface Methodology, Transesterification.

1. Introduction

India has limited crude oil reserves. India imports 70-75% of its current crude oil requirement. Transport and agriculture sectors are largely dependent on diesel fuel. Current demand of diesel is about 5 times that of gasoline. Urgent need to supplement diesel fuel to reduce dependence on imported crude oil. Biodiesel has potential to supplement diesel as fuel. The increasing prices of liquid transportation fuels, depletion of domestic petroleum reserves and growing concern about effects of fossil fuel use on global climate have led to interest in renewable alternative fuels. The use of non-edible vegetable oils compared to edible oils is very significant because of the tremendous demand for edible oils as food. Moreover, edible oils are far too expensive to be used as fuel at present.

Several methods are available for biodiesel production, the most popular being known as the transesterification reaction. During this process, the vegetable oils or animal fats are reacted with short-chain alcohols such as methanol or ethanol in the presence of an alkaline or acid catalyst to generate fatty acid methyl/ethyl esters and byproduct glycerin. Acid catalyzed esterification followed by alkaline catalyzed transesterification is more suitable for high FFA content.

As the name suggests this method uses a microwave oven to bring on the chemical reaction. Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. The application of RSM to find the optimum condition aimed to reduce the cost of expensive analysis methods and to minimize the number of experimental runs required to generate sufficient information for a statistically acceptable result. This paper is a study of the optimization of the process variables in biodiesel production by alkaline catalyzed transesterification of triglycerides from MO under microwave assisted heating. The MO with a high FFA (15.43) was processed in a two-step transesterification. The purpose of this work focused on the development of a mathematical model that could describe the effects and relationships of the process variables towards the maximum conversion to biodiesel. RSM comprising a Box Behnken method was used to evaluate the interactive effect and to obtain the optimum conditions for alkaline catalyzed transesterification of MO with respect to the methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time.

2. Materials and Methods

2.1 Materials

Mahua oil (MO) used in this project was obtained from a local oil vendor in south car street in the town of Tirunelveli city, India. The free fatty acid value of the mahua oil was calculated and the value is 15.43. The chemicals used in the experiment which include sulfuric acid (H_2SO_4), potassium hydroxide (KOH), and methanol were purchased from the Taleco chemicals, Tirunelveli city, India.

2.2 Equipment

All the experimental reactions were carried out in domestic microwave oven equipped with motorized stirrer as shown in Fig.2.1.

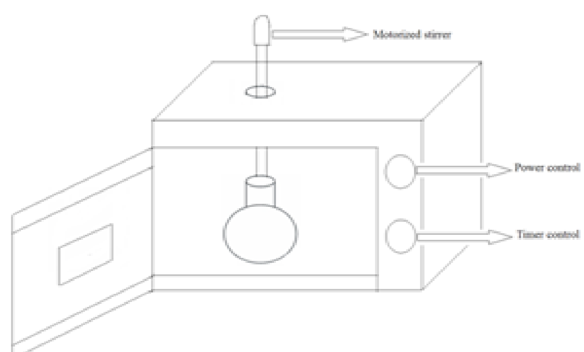

Fig.2.1 Schematic representation of experimental setup

Fig.2.2 Experimental Setup for Biodiesel Production

2.3 Pre-treatment

The mahua oil (MO) in this study contains 15.43 wt% of free fatty acid (FFA). Hence, biodiesel production from high free fatty acid oil needs a two-step transesterification process; namely, pre-treatment (acid catalyzed esterification) followed by alkaline catalyzed tranesterification to get a high yield of biodiesel. A pretreatment process was performed to lower the FFA of the feed stock. A methanol to oil molar ratio of 56% was used for the pre-treatment process using 1 ml of sulfuric acid (H_2SO_4) as a catalyst. The reaction was carried out with a microwave heating of 4 minutes with the reaction temperature of 60°C. After the acid catalyzed esterification reaction, the product was allowed to settle for 12 hrs or overnight before gum, unreacted methanol and water fraction at the top layer were removed. In this process, the FFA of the raw oil was reduced then the product was used for the alkaline catalyzed transesterification process.

2.4 Experimental design

Response surface methodology (RSM) was employed in this work to evaluate the effect of various process variables on the alkaline catalyzed transesterification process. The experimental design for this reaction was carried out by utilizing a Box-Behnken design.

A Box Behnken design with four independent variables at three levels was employed and the total numbers of experiments were 29. The chosen independent parameters for the optimization in this study were methanol to oil molar ratio (*A*), the reaction temperature (*B*), reaction time (*C*) and the catalyst concentration (*D*). The response measured was the yield (%) obtained from alkaline catalyzed transesterification of mahua oil. The range and levels of the variables investigated in this study are presented in Table (i).

Table (i) Independent variables and their levels used for response surface design

Independent variables	Levels		
A: Molar ratio (wt %)	20	30	40
B:Temperature (°C)	40	53	65
C:Time (Seconds)	30	75	120
D:Catalyst concentration (wt %)	0.5	1	1.5

Table (ii) Experimental design matrix and results

Std	Methanol to oil molar ratio A (%wt)	Reaction Temperature B (°C)	Reaction Time C (sec)	Catalyst concentration D (% wt)	Yield (%)	
					Experimental	Predicted
1	20	40	75	1.0	63	59.59
2	40	40	75	1.0	74	73.14
3	20	65	75	1.0	64	60.21
4	40	65	75	1.0	74	72.76
5	30	53	30	0.5	68	66.72
6	30	53	120	0.5	82	78.83
7	30	53	30	1.5	72	70.42
8	30	53	120	1.5	85	81.54
9	20	53	75	0.5	66	63.80
10	40	53	75	0.5	82	80.33
11	20	53	75	1.5	72	70.50
12	40	53	75	1.5	81	80.03
13	30	40	30	1.0	63	62.44
14	30	65	30	1.0	60	60.32
15	30	40	120	1.0	75	71.71
16	30	65	120	1.0	77	74.09
17	20	53	30	1.0	68	68.17
18	40	53	30	1.0	90	87.23
19	20	53	120	1.0	86	85.81
20	40	53	120	1.0	96	92.8
21	30	40	75	0.5	56	55.89
22	30	65	75	0.5	58	55.51
23	30	40	75	1.5	59	58.57
24	30	65	75	1.5	62	59.20
25	30	53	75	1.0	84	82.20
26	30	53	75	1.0	84	82.20

27	30	53	75	1.0	84	82.20
28	30	53	75	1.0	84	82.20
29	30	53	75	1.0	84	82.20

2.5 Experimental procedure

Initially, 100 ml of mahua oil was taken in a conical flask which was preheated to the oven desired temperature in a microwave oven before the reaction was started. The catalyst (KOH) was dissolved in methanol to the desired amount before the solution was added. Molar ratio of methanol to oil, reaction temperature, reaction time and catalyst concentration were set according to the values proposed in the design of the experiment as shown in Table (ii). After the reaction was completed, the reaction product was allowed to separate overnight by gravity before removing the glycerol layer from the bottom in a separation funnel. This upper phase consisted of methyl ester or biodiesel, the lower phase was glycerol. The biodiesel was washed several times with small amount of fresh hot water until the washing water was found to be neutral. Finally, the alcohol and water content was evaporated by means of heating. Then, the percentage of yield was determined.

2.6 Statistical analysis

The experimental data obtained by BBD procedures were analyzed by the response surface methodology using the second-order polynomial equation, developed to describe the relationship between the predicted response variable (yield) and the independent variable of the transesterification process. The Design Expert version 8.0.4 (STAT-EASE Inc.) software was used for graphical analysis of the experimental data. A statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The quality of the model fit was evaluated using the coefficients of determination (R^2) and a response surface plot was developed using a fitted quadratic polynomial equation obtained.

3. Results and Discussion

3.1 Model fitting and ANOVA

Table (ii) shows these experimental parameters and the results of both experimental values and predicted values on the basis of the BBD experimental design. All of the 29 designed experiments were conducted and the results analyzed. As shown in the table, the conversion to biodiesel (experimental values) ranged from 56 to 96% with the design points no.21 and no.20 giving the minimum and maximum conversion to biodiesel, respectively.

A quadratic polynomial equation was obtained from the design experimental data and the following equations were generated to predict the conversion to biodiesel yield, as shown below:

$$Y= -283.69+1.43A+10.69B+0.16C+83.07D-0.002AB-0.0067AC-0.35AD+0.002BC+0.04BD-0.011CD+0.003A^2-0.103B^2+0.0005C^2-35.33D^2 \quad (3.1)$$

Here, Y is the response variable, that is the conversion to biodiesel yield, and A, B, C, and D are the actual values, namely methanol to oil molar ratio, reaction temperature, reaction time, and catalyst concentration, respectively. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA) and to check the adequacy of the empirical model. The result of ANOVA for the selected quadratic model is summarized in Table (iii). The coefficients of the response surface model as provided by equation were also evaluated. The *p*-values (probability of error value) are used as a tool to check the significance of each of the coefficients, which also indicate the interaction strength of each parameter. According to Table (iii), the *p*-value of the model was less than 0.0001 demonstrating high significance in predicting the response values.

The quality of the model fit was evaluated by the coefficient of determination (R^2), this value being calculated to be 0.9917 for the response. This implies that 99.17% of the experimental data confirm compatibility with the data predicted by the model. The R^2 value is always between 0 and 1, and its magnitude indicates the aptness of the model. For a good statistical model, the R^2 value should be close to 1.0. The adjusted coefficient of determination (Adj. R2) value reconstructs the expression with all the significant terms included, its value of Adj. R^2 = 0.9834 also confirming that the model was highly significant.

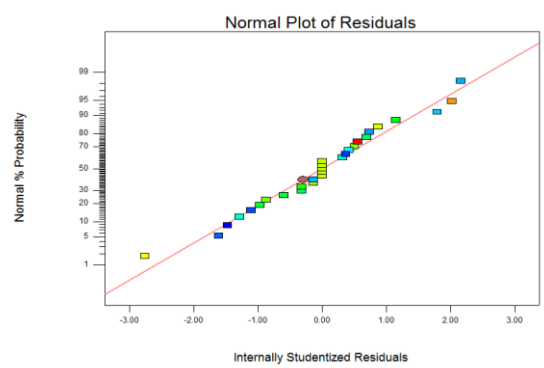

Fig.3.1 Normal probability plot of residual

The normal probability plot of residuals and studentized residuals are presented in Fig.3.1. This figure indicates that there is a characteristic dispersion of constant variables in the data. Fig.3.2 shows the actual values obtained from the experiments versus the predicted values using the model equation developed. From this figure, the pointed cluster around the diagonal line indicates a good agreement between the predicted and the experimental conversion values which prove the reliability of the model developed.

Table (iii) Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	Degrees of freedom	Mean squares	F-value	P-value
Model	3293.73	1	235.27	119.41	<0.0001 (Significant)
R^2=0.9917, Adj. R^2=0.9834, Predicted R^2=0.9522					

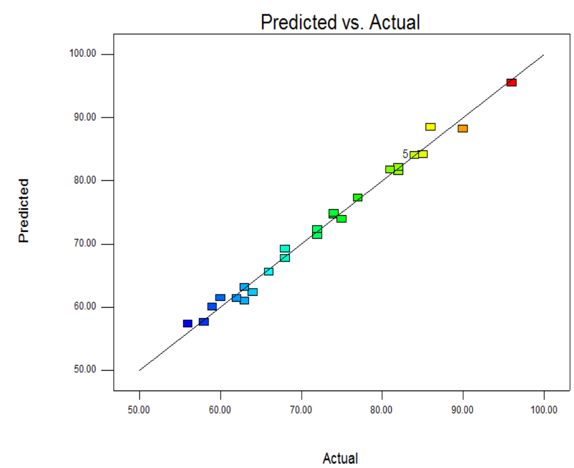

Fig.3.2 Plot of actual and predicted Value of the yield

3.2 Influence of the parameters on the conversion to biodiesel

Contour plots are graphical representation of the regression equation for the optimization of the reaction conditions. Figures 3.3 – 3.8 show contour plots between the independent and dependent variables for different fixed parameters.

The effect of varying the methanol to oil molar ratio and temperature on the biodiesel production from MO at a reaction time of 80 seconds and a catalyst concentration of 1wt % is shown in figure 3.3. It can be seen that the yield is increased with increasing in methanol to oil molar ratio reaching its peak value at a temperature of 53 ºC. Beyond this level, yield decreased. It was found that when the temperature greater than a threshold value the yield drastically decreased. Figure 3.4 shows the effect of methanol to oil molar ratio and reaction time on conversion to biodiesel at a temperature of 56 ºC and catalyst concentration of 1 wt%. In this figure, the yield increased with increasing in reaction time and increasing in methanol to oil molar ratio. As in the case, the methanol to oil molar ratio and the reaction time that were used both had a positive impact on the conversion.

Figure 3.5 shows the effect of methanol to oil molar ratio and catalyst concentration on yield at a temperature of 56 ºC and time of 80 seconds. It can be seen that the yield is increased with increasing in methanol to oil molar ratio reaching its peak value at a catalyst concentration 1 wt%. Beyond this level, yield decreased. From the figure, it can be seen that the yield increases with increase in methanol to oil molar ratio. Figure 3.6 shows the effect of temperature and time on conversion to biodiesel yield at a methanol to oil molar ratio of 30 wt% and a catalyst concentration of 1 wt%. It can be seen that the yield is increased with increasing in reaction time reaching its peak value at the temperature of 56 ºC. Beyond this level, yield increased. The yield at a threshold value of temperature after 40 seconds, conversion was found 79.7%. After 70 seconds, the conversion observed as 83.7%. After 110 seconds, the yield increased above 90%.

Figure 3.7 shows the effect of temperature and catalyst concentration on yield at a methanol to oil molar ratio of 30 wt% and a reaction time of 80 seconds. It can be seen that High yields of biodiesel are obtained at low catalyst concentrations because the reaction medium consists of a three-phase system (oil-methanol-catalyst) in which the reaction would be slowed down when the catalyst amount is high. And also yield are obtained at low temperature and then the yield decreased at higher temperatures. Figure 3.8 shows the effect of reaction time and catalyst concentration on yield at a methanol to oil molar ratio of 30 wt% and a temperature of 56 ºC. From this figure, it can be seen that the yield is increased with increasing in reaction time reaching its peak value at the catalyst concentration of 1 wt%. Beyond this level, the yield decreased. High concentration of KOH reduces the yield because of high soap formation which leads to extra processing cost because it is necessary to remove from the reaction products at the end.

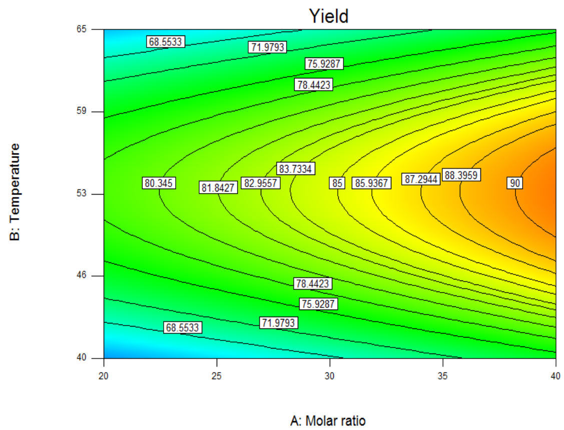

Fig.3.3 Contour plot for the effect of molar ratio and temperature on yield

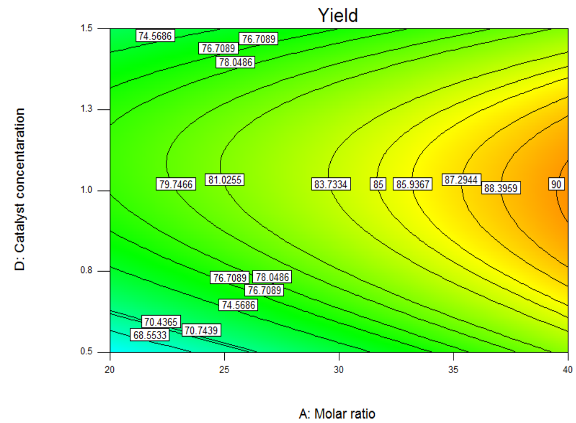

Fig.3.5 Contour plot for the effect of molar ratio and catalyst concentration on yield

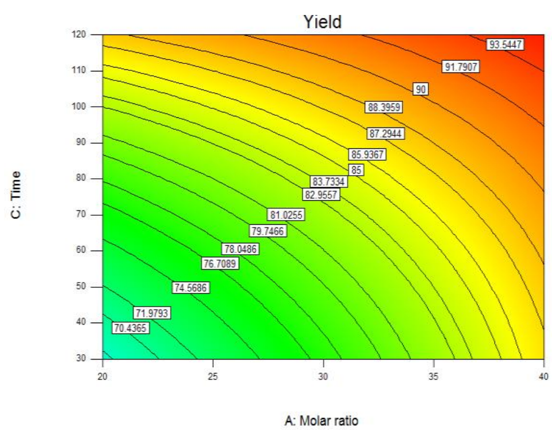

Fig.3.4 Contour plot for the effect of molar ratio and time on yield

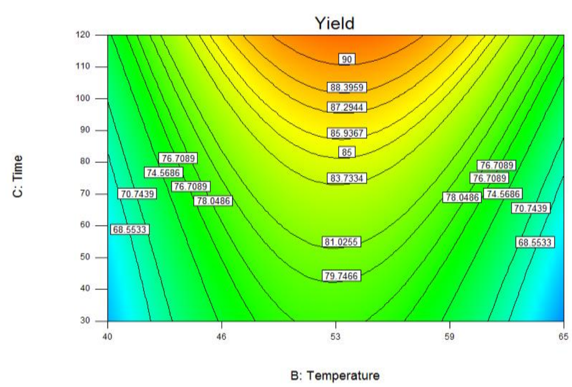

Fig.3.6 Contour plot for the effect of temperature and time on yield

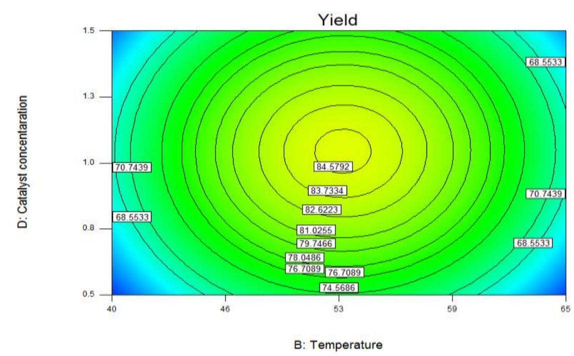

Fig.3.7 Contour plot for the effect of temperature and catalyst concentration

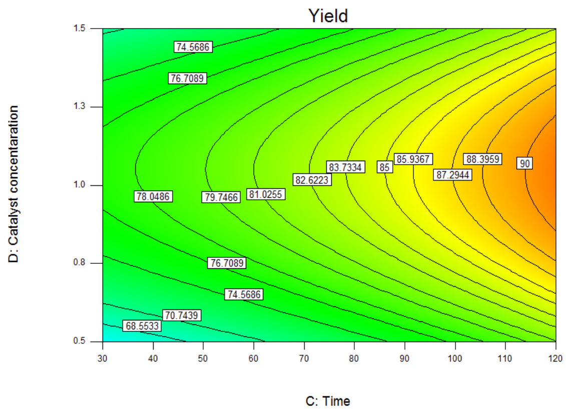

Fig.3.8 Contour plot for the effect of time and catalyst concentration on yield

4. Conclusion

The response surface methodology (RSM) method was successfully applied to the model to optimize conditions for the microwave assisted transesterification reaction parameters for biodiesel production from MO. The effect of methanol to oil molar ratio, temperature, reaction time and catalyst concentration were found to be the most significant for conversion. However, the model represents a significant step forward in predicting the yield at any point in the range of the variables. The optimum values of the parameters were methanol to oil molar ratio 40 wt%, reaction temperature 53 °C, reaction time of 120seconds and catalyst concentration 1 wt%. Under these optimum conditions, the predicted and experimental value of yield was 95.54% and 96%respectively.

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