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OPTIMIZATION OF TRANSESTERIFICATION OF YELLOW OLEANDER OIL USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

The use of edible vegetable oil as a raw material for biodiesel production gives rise to the high cost of biodiesel, which makes it more expensive than the conventional diesel. Recent biodiesel research focuses on exploring ways to reduce this high cost, especially methods concentrating on minimizing the raw material cost. The use of less expensive or non-consumable plants instead of raw vegetable oil to produce biodiesel is an effective way to bring down the cost of the raw material. This necessitates the use of non-edible oil such as *yellow oleander* oil for the production of biodiesel. This research presents the report of optimization of transesterification of *yellow oleander (*thevetia peruviana) oil using Response Surface Methodology (RSM). A central composite design (CCD) technique consisting of 28 runs was employed to study the effect of process variables: methanol to oil ratio (1:6 - 1:3), catalyst concentration (0.5 - 1.5), reaction time (30 min – 120min) and reaction temperature (50 – 60 ^oC). Statistical analysis of the variables and their interactions were carried out which lead to the development of a regression model. The maximum yield of 93.33 % was obtained at methanol-oil ratio of 1:5, catalyst concentration of 1.5g/g and reaction time of 120 min. The result of simulation of the model shows a close agreement with the experimental value.

KEYWORDS: Transesterification, RSM, yellow oleander, optimization, biodiesel.

1.0 INTRODUCTION

There is a rising substitution of fossil fuels with derivative of renewable resources. Biodiesel is one of such renewable alternative fuel derived from triglycerides by transesterification of vegetable oils and animal fats (Nie *et al;* 2006). Some of the benefits of biodiesel over conventional diesel are: biodiesel has more biodegradable properties than conventional diesel, and it also has a higher flash point and emits a very negligible amount of net greenhouse gases, such as CO_2, NO_x and sulfur to the environment. Additionally, it has higher octane number, and contains 10-11% oxygen by weight (Canakci, 2007).

Biodiesel can be produced via alkali-catalyzed transesterification reaction, acid-catalyzed esterification reaction and enzyme-catalyzed process. The first two methods are mostly adopted. The enzyme-catalyzed process requires more reaction time than the other two methods (Watanabe *et al;* 2001). Transesterification is the reaction between a lipid and an alcohol in the presence of a catalyst to form Methyl esters (FAME) and a by-product, glycerol. A reversible reaction is likely to occur, therefore an excess of alcohol is recommended to be used to enhance the reaction towards the production of fatty acid Methyl esters and glycerol (Zhang, 2003). The type of catalyst used has an effect on the yield of the reaction, by raising the rate notably. It was reported that homogeneous base catalysts such as sodium hydroxide and potassium hydroxide, carbonates and alkoxides require lesser conversion times (about 30 min) to complete the reaction even at room temperature, however homogeneous acid catalysts which include, sulfuric acid require higher temperatures (80ºC) and longer reaction times 3 to 4 hours. (Guan *et al;* 2009).

The use of virgin vegetable oil was reported to be the source of the high cost of biodiesel, which makes it more expensive than pure diesel (Lotero *et el;* 2005; Marchetti *et al;* 2007). Researchers of biodiesel have been exploring methods of reducing the high cost of biodiesel feedstock. One effective way is the use of non-edible and cheaper plants instead of virgin vegetable oil.

More also, the process of transesterification is affected by factors such as; the mode of reaction, molar ratio of methanol- to-oil, type of alcohol, type of oil, nature and amount of catalysts, reaction time and temperature (Zhang, 2003). These factors can be optimized using statistical optimization tools. Optimization of operating parameters using RSM for pre-treatment and production of biodiesel using homogeneous catalyst have been carried out by many researchers. However, there is little or no data on optimization of operating parameters for biodiesel production from yellow oleander seed oil using homogeneous catalyst. Running an experiment is a worthy way of improving any procedure. For each experimental run, design of the experiment determines which methanol- to-oil molar ratio to use, how long to react, at what temperature to operate and what concentration of catalyst to use. After running the experiments, the abilities of JMP's model fitting will be used to carried out data analysis and determine the optimal settings of the process variables studied. The objective of this study is to investigate the effects of operating parameters (methanol-to-oil molar ratio, catalyst amount, reaction time and temperature) on the transesterification of yellow oleander seed oil to biodiesel (fatty acid methyl ester) and to optimize the variables using RSM.

Response Surface methodology (RSM), introduced by Box and Wilson (Box L. and Wilson, K.B., 1951) is a group of methods that were developed as a way of determining optimal settings for input factor or design parameter that maximize, minimize or target measured responses or outcome variables.

The mathematical illustration of RSM models are expressed in eqn. (1) through eqn. (3):
For first-order (linear) model without interaction or cross product term:

$$Y(x) = b_0 + \sum_{i=1}^{k} b_i x_i + e \qquad (1)$$

For first-order (linear) model with interaction or cross product term:

$$Y(x) = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{j=2}^{k} \sum_{i=1}^{j=1} b_{ij} x_i x_j + e \qquad (2)$$

The second-order (quadratic) model:

$$Y(x) = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{j=2}^{k} \sum_{i=1}^{j=1} b_{ij} x_i x_j \sum_{i}^{k} b_{ij} x^2 + e \qquad (3)$$

According to Cornell, models can be fitted with RSM to: (i) Screen for the most significant factors affecting the response (most screening designs stop at this point); (ii) Find the region of the factor space that can be approximated reasonably well by the RSM model; (iii) Obtain an initial approximation of the surface in the simplest possible model to minimize the time and cost of experimentation; (iv) Develop a sequential technique that tries to detect more desirable values of the response (Cornell 1990).

2.0 MATERIALS AND METHODS

Mature fruits of Thevetia peruviana (Yellow Oleander) plants were handpicked from Maiduguri, Borno State (Nigeria). The fruits were then continuously dried under the sun to remove the remaining moisture. The black pericarp was separated from their stony kernel by pounding in a mortar. The stony kernels were cracked with an iron nail to remove the nut inside the kernels. Subsequently, the seed nuts were grounded using manual grinding machine to increase the surface area of the sample and also weaken the cells to enhance oil extraction. Some of the grounded seed was placed in a bowl and hot water was added, stirred and pressed continually using bear hands, until oil was obtained. The process was repeated until reasonable amount of oil was obtained. The extracted oil was filtered with a filter paper to get rid of solid impurities.

2.1 EXPERIMENTAL PROCEDURES

The following procedures were adopted for all process parameters involved in the synthesis of biodiesel from yellow oleander seed oil:

a) The experiment was carried out in a water bath; water in the bath was heated to the designed temperature.
b) 10 ml of Thevetia peruviana oil was measured in a 20 ml measuring cylinder and heated to a specified temperature.
c) Specified amount of methanol was measured in a 10ml measuring cylinder.
d) Potassium hydroxide was weighed and dissolved in the measured methanol in a dry conical flask to form methoxide. The conical flask was sealed throughout the dissolution process to limit the evaporation of methanol and absorption of moisture by the mixture.
e) The alcoholysis reaction was performed in a 50ml glass jar fitted with a mechanical stirrer at a constant speed of 300rpm.
f) The preheated Yellow oleander seed oil (10ml) was placed into the reaction flask and the prepared methoxide was further added.
g) At the termination of the reaction time, the crude mixture was transferred into a separating funnel where it was allowed to separate for 24 hours. The mixture separated into two layers; crude glycerol, the heavier liquid, is collected at the bottom and the lighter liquid which was the methyl ester (biodiesel).
h) The crude biodiesel was washed with warm water in the ratio 2:1 (biodiesel to water). The washing was repeated until the wash water was clear. The mixture was allowed for a few minutes to settle and the heavier wash water at the bottom was drained off. The biodiesel was then collected in a beaker and the remaining water trapped in the biodiesel was heated off on a hotplate in the drying stage. The volume of the biodiesel after washing and dried was recorded and stored in 20ml plastic bottles.
i) The yield of biodiesel was determined using the equation (4):

$$\text{Yield of Biodiesel} = \frac{\text{volume of biodiesel produced}}{\text{volume of oil used}} \quad (4)$$

2.2 Design of Experiment for Biodiesel Production

JMP statistical Analysis software, version 13.0 was used in the design of experiment for this work. RSM design with four factors and one response was applied with a total number of 28 runs. From literature and previous work done, the factors that shows significant influence on the biodiesel yield are; temperature (ºC), catalyst concentration (wt %), time of reaction (min) and methanol: Oil ratio (v/v) and the response was the yield of biodiesel which was obtained using equation 4 (Ghadge SV and Raheman H., 2006). The four factors were varied on various levels to design the experiment as outlined in Table 1.

Table 1: Experimental range and levels of the independent variables.

Factors	**Low**	**High**
Methanol-to-oil ratio	3:1	6:1
Catalyst, (%)	0.5	1.5
Reaction time, (min)	30	120
Reaction Temperature (^{o}C)	50	60

The operational matrix for these settings was prepared using the above factors for all the 28 runs, as shown in Table 2. Each response obtained from the transesterification process was used in developing a mathematical model using RSM that correlates the biodiesel yield to the independent process. The quality of the developed model was determined from the value of correlation while evaluation of the statistical significance of the equations developed was determined using an analysis of variance (ANOVA).

3.0 RESULTS AND DISCUSSION

The complete design matrix of the experiments coupled with the experimental yield and predicted yield is presented in Table 2. From the table, it can be seen that the biodiesel yield obtained was in the range of 62% to 90.70%.

Table 2: The Full Factorial design for optimizing transesterification Process.

	Operational Matrix				**Response**	
Runs	**Temperature (oC)**	**Catalyst Conc. (g/g)**	**Time (min)**	**Methanol: Oil**	**Biodiesel Yield Actual**	**Biodiesel Yield Predicted**
1	50	0.5	30	3:1	0.61	0.61
2	50	0.5	30	6:1	0.65	0.63
3	50	0.5	120	3:1	0.81	0.81
4	50	0.5	120	6:1	0.80	0.83
5	50	1.5	30	3:1	0.70	0.7
6	50	1.5	30	6:1	0.72	0.72
7	50	1.5	75	4:1	0.83	0.82
8	50	1.5	120	3:1	0.85	0.84
9	50	1.5	120	6:1	0.85	0.86
10	55	0.5	30	4:1	0.70	0.68
11	55	1	75	3:1	0.75	0.76
12	55	1	75	3:1	0.75	0.76
13	55	1	75	4:1	0.80	0.81
14	55	1	75	5:1	0.80	0.82
15	55	1	75	6:1	0.81	0.78
16	55	1	75	3:1	0.78	0.76
17	55	1.5	120	5:1	0.86	0.91
18	55	0.5	120	6:1	0.85	0.85
19	60	0.5	30	3:1	0.61	0.64
20	60	0.5	30	6:1	0.62	0.66
21	60	0.5	75	5:1	0.81	0.8
22	60	0.5	120	3:1	0.86	0.85
23	60	1	30	5:1	0.79	0.75
24	60	1	120	6:1	0.91	0.88
25	60	1.5	30	3:1	0.70	0.73
26	60	1.5	30	6:1	0.74	0.75
27	60	1.5	75	6:1	0.85	0.82
28	60	1.5	120	3:1	0.89	0.87

Table 3 indicated that the fitted models are responsible for more than 94 percent of the variation in the biodiesel yield. The Parameter Estimates showed the coefficients and significance of the linear, cross-product, and quadratic terms on each response. A second-order (quadratic) model with respect to methanol only without the cross-product term except for Catalyst-Time combination seemed to fit the biodiesel yield. According to the sequential model sum of square, the best model to fit the response was quadratic model due to its highest order polynomial with significance of additional terms. The final model equation for the biodiesel yield is expressed as:

$$Y = 0.227 + 0.034T + 0.058C + 0.00191t + 0.057C + 0.00076t * C + 0.1087M - 0.0227M^2 \quad (5)$$

Where Y is the biodiesel fractional yield whereas t, C, M and T represent reaction time, catalyst concentration, methanol-to-oil molar ratio and reaction temperature respectively.

Table 3: Summary of Fit and Parameter Estimates.

RSquare	0.949541
RSquare Adj	0.895201
Root Mean Square Error	0.027194
Mean of Response	0.774629
Observations (or Sum Wgts)	28

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**	**Lower 95%**	**Upper 95%**
Intercept	0.8254778	0.013808	59.78	<.0001*	0.7956476	0.855308
TEMP.(50,60)	0.015501	0.006567	2.36	0.0346*	0.0013129	0.0296891
CATALYST(0.5,1.5)	0.0274588	0.006227	4.41	0.0007*	0.0140057	0.0409119
TIME(30,120)	0.0869924	0.006415	13.56	<.0001*	0.0731334	0.1008513
METH:OIL(3,6)	0.0109385	0.005908	1.85	0.0169	-0.001825	0.0237019
METH:OIL*METH:OIL	-0.053596	0.015122	-3.54	0.0036*	-0.086266	-0.020927
TEMP.*CATALYST	0.0021248	0.006847	0.31	0.7612	-0.012668	0.0169173
TEMP.*TIME	0.0122486	0.006971	1.76	0.1024	-0.002812	0.0273096
TEMP.*METH:OIL	0.0044178	0.006961	0.63	0.5366	-0.01062	0.0194553
CATALYST*TIME	-0.015405	0.00683	-2.26	0.0420*	-0.030161	-0.000649
CATALYST*METH:OIL	0.0009295	0.006749	0.14	0.8926	-0.01365	0.0155094
TIME*METH:OIL	-0.004346	0.006901	-0.63	0.5398	-0.019255	0.0105631
TEMP.*TEMP.	0.019175	0.015285	1.25	0.2317	-0.013846	0.0521961
CATALYST*CATALYST	-0.020864	0.015826	-1.32	0.2101	-0.055053	0.0133248
TIME*TIME	-0.004514	0.014712	-0.31	0.7638	-0.036297	0.0272681

3.1 Effect of Individual Parameters on the Biodiesel Yield

From Figure 1, it can be seen that the catalyst concentration has significant effect on biodiesel yield in a positive way up to a concentration (1.5g/g). Above this concentration, the biodiesel yield remains constant. When the catalyst concentration was increased, the interactive (active) site of the catalyst was increased; thus, the transesterification reaction was enhanced and biodiesel yield increases.

The increase in reaction time increases biodiesel yield linearly as shown in Figure 1. Within the range of reaction time set for the experiment, biodiesel yield increases continuously. The increase in the yield of biodiesel at higher reaction time is as a result of higher reaction rate. Hence, its effect on the biodiesel is nearly constant.

According to the reaction stoichiometry, for every one mole of triglyceride, three moles of methanol are required. But in reality, a higher molar ratio is required in order to drive the reaction forward towards completion and produce more biodiesel (FAME) as products.

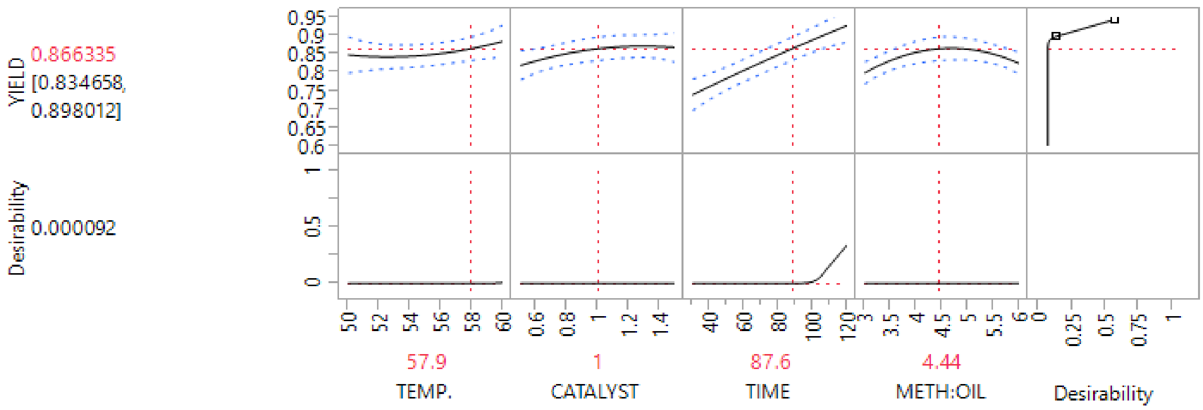

Figure 1.0: Prediction profile for the process variables.

It can be seen from Figure 1 that the methanol-to-oil ratio has positive effect on biodiesel yield. But further than ratio 5:1, the yield started to decrease. The decrease in the yield may be attributable to separation difficulties as a result of excessive methanol. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst active sites which could decrease the catalyst activity.

Biodiesel yield increases gradually as temperature increase. From Figure 1, it is obvious that temperature is the least significance of all the process variables. Desirability tools of the JMP Software was use to set the optimal variables that give the highest yield as presented in Figure 2, with the operating variables of 60^{o}C, 1.5, 120min, and 4.7 (≈5:1) for reaction temperature, catalyst concentration, time and methanol:oil ratio respectively.

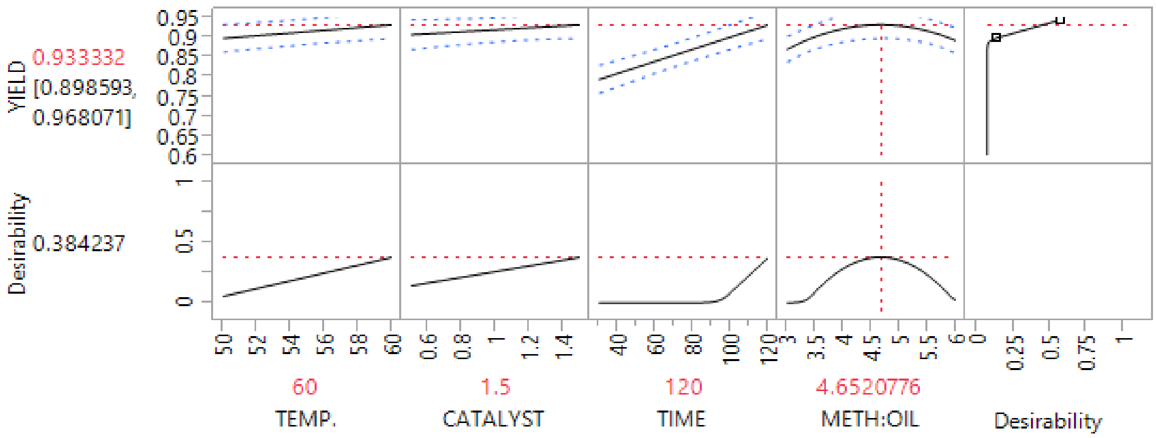

Figure 2: Prediction profile for optimum operating conditions.

3.2 Effect of Interactive Parameters on the Biodiesel Yield

Combination of catalyst and time was the only interactive parameter that is significant in affecting the yield of biodiesel as observed as indicated in Table 3. The interaction of these parameters can be visualized in Figure 3, keeping reaction temperature and time fixed.

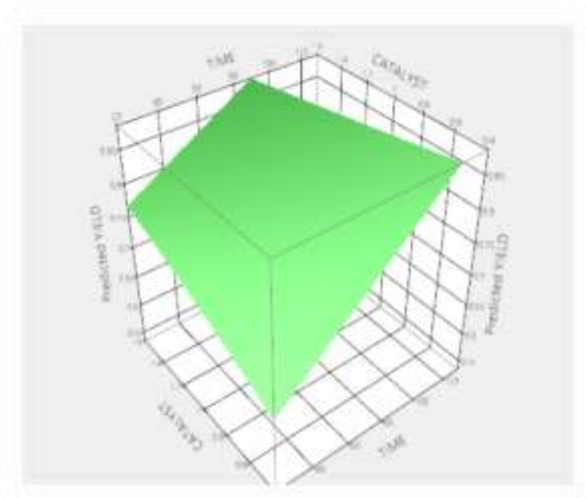

Figure 3: Catalyst Concentration and Reaction Time at fixed Temperature and Methanol: Oil.

Figure 3 shows the strong interaction between reaction time (t) and catalyst concentration (C). The high p-values of the interaction parameters (Table 3) confirms this strong interaction. Figure 3 also shows that as the catalyst concentration increases, the biodiesel yield also increases. However, as time increases with increase in catalyst concentration the yield increases rapidly. The reverse trend was indicated by decrease in the yield. This was because the positive coefficient for the quadratic parameters (t*C) has the most significant effect in increasing the yield. However any increment in the catalyst concentration above the optimum value (1.5g/g) could result in the formation of soap which will invariably reduce the yield of the biodiesel produced.

4.0 CONCLUSSIONS

Response Surface Methodology was successfully employed in studying the effects of operating parameters, such as reaction temperature, methanol-oil ratio, catalyst concentration and reaction time for the production of biodiesel from the yellow oleander oil. An empirical model equation was developed for the biodiesel (methyl esters) yield as a function of the variables investigated. The experimental results show that the optimal conditions were as follows: reaction temperature of 60^{o}C, methanol/oil molar ratio of 5:1; time of 120 min; catalyst concentration, of 1.5%. The optimized condition gave an actual yield of 93.33%. All the individual process variables show a positive effect on biodiesel yield.

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