

Optimization of Mahua Oil Methyl Ester by using Response Surface Methodology

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Abstract--- The most commonly used methods for biodiesel preparation is via transesterification of vegetable oil using alkaline catalysts. The transesterification process can be affected by differing parameters. The optimization of experimental parameters, such as oil to alcohol molar ratio, catalyst concentration and reaction time, on the transesterification for the production of Mahua oil methyl ester in Oscillatory Baffled Reactor has been studied. The biodiesel production was optimized by response surface methodology. The optimum condition for the predicted condition product yield is 92.7157 ml with 1:12 of methanol to oil molar ratio, 0.4 wt of catalyst concentration and 10 minutes of reaction time.

Keywords: Biodiesel, response surface methodology, Mahua oil, Transesterification reaction, Oscillatory Baffled Reactor

I. INTRODUCTION

There has been renewed interest in the utilization of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional diesel, which is a fossil fuel leading to a potential exhaustion^[1]. One of the most interesting alternatives of the renewable fuels, among others, is the vegetable oil fuel for diesel engine. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon-based diesel fuels. The problems with substituting vegetable oil for diesel fuels are largely associated with their high viscosities, low volatilities and polyunsaturated character^[2].

Vegetable oil fuel, or biodiesel, is a likely substitute for diesel fuel because it is produced from renewable sources. In the American Society for Testing and Materials (ASTM) biodiesel fuel is defined as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat^[3].

Commonly used feed stocks (vegetable oil) for transesterification include soybean oil, rapeseed oil, etc. In recent years, there exist active researches on biodiesel production from Mahua oil^[4,5].

Response surface methodology (RSM) is a useful statistical technique, which has been used in the research of complex variable processes. Multiple regression and correlation analysis are used as tools to evaluate the effects of two or more independent factors on the dependent variables. Furthermore, the central composite design (CCD) of RSM has been utilized in the optimization of several biotechnological and chemical processes. Its main advantage is the reduction in the number of experimental runs required to generate sufficient data for a statistically acceptable result^[6]. RSM has been used successfully for optimization of biodiesel production in fat and oil feedstock, including

Mahua oil (*Madhuca indica*)^[1], cotton seed oil *Jatropha* oil^[7], palm oil^[8].

The objectives of this paper are to investigate the interaction effects among process variables for biodiesel production from Mahua oil and to optimize the process conditions for maximum FAME yield in the presence of various catalysts. The methanol to oil molar ratio, catalyst concentration and reaction time are four variables pertaining to the biodiesel production since these variables significantly affected the process. Response surface methodology (RSM) was used to relate these three process variables with the response (biodiesel yield) and to determine the optimal combination of process variables that would maximize the biodiesel yield.

II. MATERIALS AND METHODS

A. Materials

Madhuca longifolia, commonly known as mahwa or Mahua, is an Indian tropical tree found largely in the central and north Indian plains and forests. The two major species of genus *Madhuca* found in India are *Madhuca Indica* (*latifolia*) and *Madhuca longifolia* (*longifolia*). The seed potential of this tree in India is 500,000 tons and oil potential is 180,000 tons. It is a fast-growing tree that grows to approximately 20 meters in height, possesses evergreen or semi-evergreen foliage, and belongs to the family Sapotaceae. It is found in India in the states of Chhattisgarh, Jharkhand, Uttar Pradesh, Bihar, Maharashtra, Madhya Pradesh, Kerala, Gujarat and Orissa. Oil content in *latifolia* is 46% and 52% in *longifolia*. In seeds oil content is 35% and protein at 16%^[9].

B. Production of Mahua Oil Methyl Ester

The set of experiments was constructed and randomly conducted to evaluate the three factors such as oil to alcohol molar ratio, catalyst concentration and reaction time. Oscillatory baffled reactors are used in biodiesel production, it consisting of tube containing equally spaced orifice plate baffles. An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficiently heat and mass transfer, whilst maintaining plug flow^[10]. The reactions were carried out in Oscillatory Baffled Reactor at room temperature 25^oC to 30^oC. The speed of the oscillation was fixed at 138 r/min for all experiments.

1) Step – 1: Esterification of Mahua Oil (Pretreatment)

The pretreatment process comprised of two steps. In each step, different methanol-to-oil ratios and sulfuric acid as a catalyst (5 v/v %) by varying reaction time at room temperature i.e. 25^oC - 30^oC were used to investigate their influence on the acid value of crude Mahua oil. Then, the mixture was left overnight to settle into two layers. The lower layer was removed while the upper layer which contained fatty acid methyl ester and un-reacted

triglycerides were subjected to the second step of transesterification process.

2) Step – 2: Transesterification

In the second stage, treated Mahua oil obtained from first stage was transesterified in an Oscillatory Baffled Reactor by varying the oil-methanol molar ratio with various catalysts (KOH, NaOH, NaOCH₃) having reaction time of 10min and temperature 25^oC to produce methyl ester. Eventually, the mixture was left overnight to settle into two distinct layers i.e. glycerol layer and methyl ester Layer. Upper layer of methyl ester is separated and is preserved for analysis. To optimize the above transesterification process, a three level three factor (2³) fractional factorial experimental design was employed (Table I).

Parameters		Levels		
		1	2	3
A	Molar ratio (oil/methanol)	1:9	1:12	1:15
B	Catalyst type	KOH	NaOH	NaOCH ₃
C	Catalyst conc. (wt %)	0.3	0.4	0.5
D	Reaction time (min)	5	10	15

Table. 1: Design Experiments, With Four Parameters At Three-Level, For The Production Of Mahua Methyl Esters

C. Analysis

The composition of methyl ester in the Pre Treatment and transesterification was analyzed by using gas chromatography by using GCMS-MS Test method. The capillary column is TR Wax MS (30m × 0.25mm × 0.25um) and helium was used as carrier gas. The operating oven temperature is 280^oC. The other properties checked were the acid value, density, viscosity in laboratory and calorific value by using IS: 1350(Part 2): 1970 Test method. The optimal condition was analyzed by using LAB FIT software and Design Expert 8.0 Software.

III. RESULT AND DISCUSSION

A. Optimization process

The optimization of a chemical process i.e. biodiesel using Response Surface Methodology follows the statistical approach which involves three major steps. They are selected of designing experiments, estimation of coefficients based on mathematical models and response prediction

along with the conformation of mathematical model adequacy^[11].

B. Experimental Design

Three level variables were employed in this study, requiring 27 experiments. Methanol-to-oil ratio, catalyst concentration and reaction time were the independent variables selected to optimize the yield of Mahua oil after transesterification. A response surface methodology (RSM) was used to examine the influence of these three process variables on the fatty acid methyl esters (FAMEs) content. This methodology is a sequential process that usually originates at one reasonable operating condition, and then requires three points to achieve a set of “better” conditions as rapidly and efficiently as possible.

First of all we are working on software LAB FIT for finding the LINEAR, CROSS and SQUARE VALUE for Natural variables. Now we will proceed in determining the value of Yield on the basis of linear equation. Firstly select the number of independent variable i.e. Molar Ratio (X1), Catalyst Concentration (X2) and Reaction Time (X3). Put the value of independent variable when the software provides the data sheet. Next assign the value of Y i.e. Yield. The value of X1, X2, X3 and Y is saved by the software. Now we will select the toolbar of curve fitting in the software and develop the equation for Linear Equation as below. This all value are Developed by RSM software by using the independent equation for finding the value of Y i.e. Yield for all Runs. i.e. 27 number Runs (shown in Table II).

Further we need the square equation model to find the best 20 Runs in Design Expert 7 software. The best 20 runs are the developed by the software which provide the same optimum condition and 3D graph which is tantamount to the same condition and graph which can be obtained by using the 27 number of practical experimental runs. We have to supply the data, Molar Ratio (X1), catalyst Concentration (X2) and Reaction Time (X3). The next software

predicts the value of Y from the equation i.e. Yield. The software will develop the best 20 Runs suitable for the above parameters. The best 20 runs final sheet provided by the software is demonstrated in Table III

Mahua Oil Methyl Ester (MOME) 2 nd Stage										
Run No.	Natural Variable				Coded Variable			Linear	Cross	Square
	Molar Ratio	Catalyst Concentration n(Wt)	Reaction Time (min)	Yield	Molar Ratio	Catalyst Concentration n (Wt)	Reaction Time (min)			
	X1	X2	X3	Y	X1	X2	X3			
1	9	0.3	5	94.19	1	1	1	92.09111	94.76778	95.44
2	9	0.4	10	93.94	1	0	0	92.06611	92.69159	94.99
3	9	0.5	15	74.5	1	-1	-1	92.04111	88.11349	86.86667
4	12	0.4	15	93.25	0	0	-1	91.92778	92.33111	95.02
5	12	0.5	5	93.94	0	-1	1	93.17945	96.92587	95.77667
6	12	0.3	10	90.2	0	1	0	91.95278	89.05397	84.06667

7	15	0.5	10	93.88	-1	-1	0	93.04111	96.12111	94.77667
8	15	0.3	15	93.11	-1	1	-1	91.81444	94.9354	95.51
9	15	0.4	5	90.3	-1	0	1	93.06611	86.23968	88.73333
10	9	0.3	5	94.47	1	1	1	92.09111	94.76778	95.44
11	9	0.4	10	94.15	1	0	0	92.06611	92.69159	94.99
12	9	0.5	15	94.6	1	-1	-1	92.04111	88.11349	86.86667
13	12	0.4	15	94.01	0	0	-1	91.92778	92.33111	95.02
14	12	0.5	5	94.19	0	-1	1	93.17945	96.92587	95.77667
15	12	0.3	10	83.8	0	1	0	91.95278	89.05397	84.06667
16	15	0.5	10	94.09	-1	-1	0	93.04111	96.12111	94.77667
17	15	0.3	15	93.77	-1	1	-1	91.81444	94.9354	95.51
18	15	0.4	5	91.5	-1	0	1	93.06611	86.23968	88.73333
19	9	0.3	5	97.66	1	1	1	92.09111	94.76778	95.44
20	9	0.4	10	96.88	1	0	0	92.06611	92.69159	94.99
21	9	0.5	15	91.5	1	-1	-1	92.04111	88.11349	86.86667
22	12	0.4	15	97.8	0	0	-1	91.92778	92.33111	95.02
23	12	0.5	5	99.2	0	-1	1	93.17945	96.92587	95.77667
24	12	0.3	10	78.2	0	1	0	91.95278	89.05397	84.06667
25	15	0.5	10	96.36	-1	-1	0	93.04111	96.12111	94.77667
26	15	0.3	15	99.65	-1	1	-1	91.81444	94.9354	95.51
27	15	0.4	5	84.4	-1	0	1	93.06611	86.23968	88.73333

Table. 2: Pre-Treatment Stage Optimization Of Neem Oil

C. Statistical Analysis

The experimental data obtained by following the above procedure were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$Y =$$

$$\beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i < j=1}^3 \beta_{ij} x_i x_j \dots\dots (1)$$

Where Y is the response (Yield); X_i and X_j are the uncoded independent variables and β₀, β_i, β_{ii} and β_{ij} are intercept, linear, quadratic and interaction constant coefficients respectively. SPSS package was used for regression analysis and analysis of variance (ANOVA). Response surfaces and contour plots were produced using the fitted quadratic polynomial equation obtained from regression analysis, taking one of the independent variables at a constant value corresponding to the stationary point and changing the other two variables. Confirmatory experiments were carried out to

validate the equation, using combinations of independent variables which were not part of the original experimental design but within the experimental area.

Now we will apply the software Design Expert 7.0 for analysis the variance in order to determine that the observational data is adequate and fits the mathematical model. Figure 1 compares the observed experimental product yield with predicted product yield. The R² value of the product yield is 0.545665 i.e.54.5665% of the variability in the data is accounted to the model.

D. Relationship of manipulated variable

The empirical model has been plotted in a 3D surface which represents the response i.e. product yield as factor of function of two experimental variables (Fig. 2-4). The relationship between molar ratio and catalyst concentration at time 10 min is shown in Figure 2.

Run No.	Molar Ratio(X1)	Coded X1	Catalyst Concentration (X2)	Coded X2	Reaction Time (X3)	Coded X3	Yield
1	12	0	0.4	0	10	0	92.71567
2	12	0	0.4	0	10	0	92.71567
3	15	-1	0.3	1	5	1	77.50456
4	12	0	0.4	0	10	0	92.71567
5	17.04538	-1.68179	0.4	0	10	0	97.14416
6	9	1	0.5	-1	5	1	104.3412
7	9	1	0.5	-1	15	-1	86.86667
8	9	1	0.3	1	5	1	95.44

9	12	0	0.4	0	10	0	92.71567
10	9	1	0.3	1	15	-1	83.8183
11	15	-1	0.5	-1	15	-1	103.0246
12	12	0	0.231821	1.681793	10	0	72.95832
13	15	-1	0.5	-1	5	1	90.87199
14	12	0	0.4	0	10	0	92.71567
15	15	-1	0.3	1	15	-1	95.51
16	12	0	0.4	0	1.591036	1.681793	98.6347
17	6.954622	1.681793	0.4	0	10	0	98.63889
18	12	0	0.4	0	18.40896	-1.68179	99.08111
19	12	0	0.4	0	10	0	92.71567
20	12	0	0.568179	-1.68179	10	0	86.7623

Table 3: Best 20 Runs Provided By The Software

The Figure 2 shows that yield decrease when catalyst concentration is more and yield increases with decreasing catalyst concentration. Similarly, with increase in molar ratio the yield of product increases and with less molar ratio the yield decreases.

Figure 3 shows the response surface plot of yield as a function of reaction time and molar ratio. As the reaction time increases the yield of product increases and with less time the yield also decreases. Similarly the response plot shows that as the molar ratio increases the yield of product increases.

Figure 4 shows the various effects of catalyst concentration and reaction time on the yield of product. As the reaction time increases, the yield of the product decreases. Similarly as the catalyst concentration goes on increasing the yield of product goes on increasing.

E. Optimization analysis

The response surface analysis using Design Expert 7.0 software indicated that the optimum condition for the predicted condition product yield is 92.7157 ml with 1:12 of methanol to oil molar ratio, 0.4 wt of catalyst concentration and 10 minutes of reaction time.

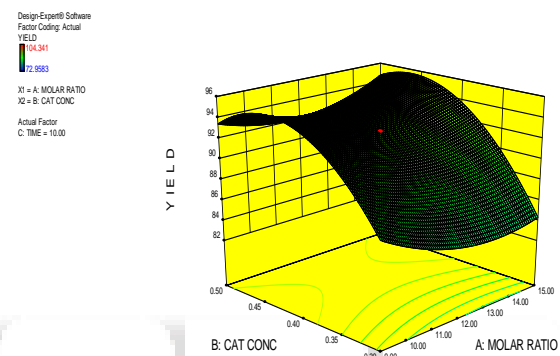


Fig. 2: 3 D Graph For Catalyst Conc. Vs Molar Ratio For Yield

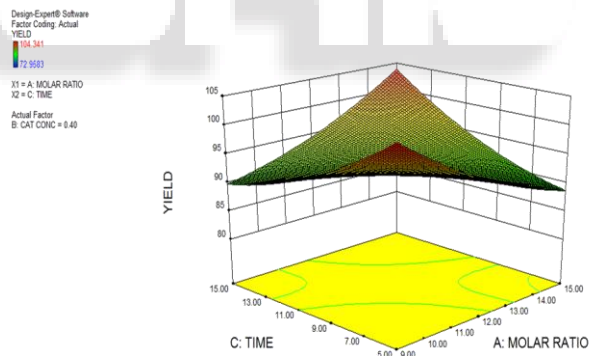


Fig. 3: 3d Graph For Reaction Time Vs. Molar Ratio For Yield

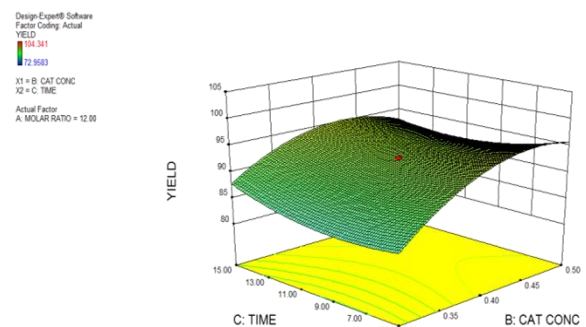


Fig. 4: 3d Graph For Reaction Time Vs Catalyst Conc. For Yield

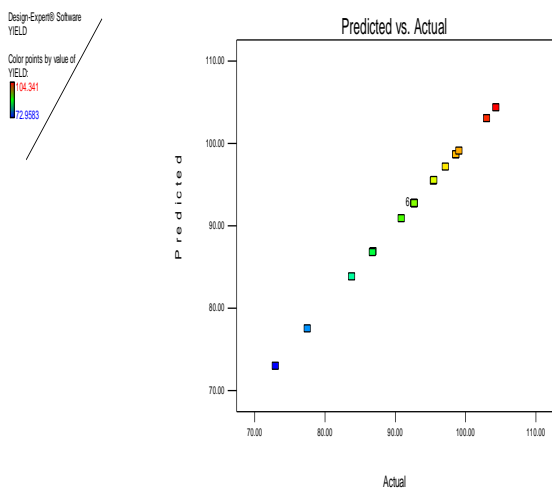


Fig. 1: Pairing Plot For Observed And Predicted Product Yield

IV. CONCLUSION

The Response surface methodology and central composite design optimization tool is effective to determine the optimum condition for the process and the interconnected relationship. Also a second order model was obtained to predict yield as a function of methanol-to-oil ratio, catalyst concentration and reaction time. The model was found to describe adequately the experimental range studied. The optimum condition for the predicted condition product yield is 92.7157 ml with 1:12 of methanol to oil molar ratio, 0.4 wt of catalyst concentration and 10 minutes of reaction time.

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