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Study on Optimization of Cottonseed oil Transesterification Process

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Abstract : In this work, optimization of the parameters that affects the cottonseed oil transesterification process with methanol and Potassium Hydroxide (KOH) catalyst is studied. The impacts of three factors (molar ratio, amount of catalyst and reaction time) on the percentage of biodiesel yield produced from the cottonseed oil were considered. The process of transesterification was optimized by using the box-behnken design approach of response surface methodology (RSM). The seventeen experimental runs were generated by box-behnken design. With methanol, each experimental run was performed in 1000ml batch reactor. The results attained from the experimental runs were modelled and analyzed by choosing a quadratic model. The results obtained from the analysis of variance (ANOVA) of the model developed for the percentage yield of biodiesel as a function of molar ratio, amount of catalyst and reaction time. From the ANOVA, it was found that the polynomial model and the three linear terms, (A, B, C), one cross product (AB), and one quadratic term (A^2) are more significant because of their probability values (p-value)were identified to be less than 0.05 that was chosen based on the 95% confidence level. From statistical summary of quadratic model, it was observed that the predicted R-squared of 0.9331 is in feasible range with the adjusted R-squared value of 0.9835. The impacts of molar ratio ,catalyst concentration, and reaction time in relation to yield of biodiesel at constant reaction temperature of 65°c were investigated and optimized. Finally, the optimization results indicated 92.37% of biodiesel yield at molar ratio of 5:1 catalyst concentration of 0.7 (wt%), and reaction time of 2 hrs. The optimized condition was verified with the actual yield of 91.5%. Thus, it can be presumed that RSM under Box-Behnken design has been used successfully in optimization of cottonseed oil transesterification process.

Keywords : Optimization, Transesterification, Catalyst, Biodiesel, RSM, Box-Behnken Design etc.

1.0 Introduction

The larger sector of the world's energy needs are provided through petrochemical assets, for example, coal and natural gasses, except for nuclear energy and hydroelectricity. These reserves are constrained and at current usage rates, will be exhausted shortly. The fast industrialization and motorization of the world has prompted to a precarious ascent for the demand of petroleum based products. These reserves are extremely located in certain zones of the world. Those nations which are not having these reserves are confronting a foreign exchange crisis, because of the import of raw petroleum products. At present, the world is facing the

worst energy crisis in history. Most of the countries worldwide are still strongly dependent on petroleum resources as their main source of electricity and transportation fuel. Its cost has been setting record highs as of late. Consequently, the unrivaled solution to this crisis is to find a sustainable (non-conventional) and monetarily practicable source of alternative energy. There are many alternative (non-conventional) energy sources for example wind, solar, geothermal, OTEC (Ocean Thermal Energy Conversion) and biomass which fulfill the first criterion (sustainability). But a few of these can fulfil the second criterion (monetary practicability). Therefore, the best option, fulfilling the above, two criterions, is bio-fuel, especially that are made readily accessible from biomass feed stocks. Subsequently it is important to search for substitute fuel, which can be composed from materials available within the country. [1-3]

The biodiesel has emerged as one of the most promising alternatives to petroleum based diesel. It offers the following advantages: bio- degradable, non toxic, renewable, higher cetane number and environmental friendly. Biodiesel is typically produced from vegetable oils or animal fats via transesterification process [4].Transesterification is also called alcoholysis, it requires alcohol and catalysts for converting vegetable oils, or animal fats in to fatty acid methyl or ethyl esters. The commonly used alcohols for the transesterification process include, methanol, ethanol, butonal and proponal. Methanol is commonly adopted due to its lower cost. The feedstocks used for biodiesel production include edible and non-edible vegetable oils. The generally used vegetable oils (edible) are soybean, sunflower, coconut and palm oil etc. The usage of the edible oils has the various disadvantages include depletion of food supply, high cost etc. Now a days these oils are replaced by non-edible oils such as karanja (Pongamia pinnata.L), Polanga (Calophyllum inophyllum), Mahua (Madhuca indica) Rubber seed oil (Hevea brasiliensis), Jatropha (JatrophaCurcas L),Neem (Azadirachta indica) and Cotton seed oil(Gossypium hirsutum) etc. [5-7].

Regardless of the feedstock used for biodiesel production, a catalyst is required to complete the process in a reasonable time. In other words, a catalyst is essential to improve the reaction rate and yield. The catalyst is not desired for biodiesel synthesis in the case of alcohol and oil are used in supercritical conditions. The conventional catalysts used are homogeneous and heterogeneous catalysts depending upon the nature of feedstock used for the biodiesel production. Another catalyst being studied is biocatalyst (lipase). [8].There are many studies of the alcoholysis of triglycerides using homogeneous catalysts [9-11]. For homogeneous catalysts, eminent conversions are easy to acquire in lesser than an hour of reaction at temperatures from 40 to 65 °C [12]. Moreover, the transesterification procees is strongly influenced by several factors including free fatty acid content in feedstocks, molar ratio of oil to alcohol, catalyst concentration, stirring speed, reaction time, and temperature. [13].Optimization study for biodiesel production is important to assist researchers to establish a most adequate and cost effective-system in biodiesel industry. [14]. The optimization studies of transesterification process using Response Surface Methodology (RSM) has been carried out by the researchers [15-22]. Therefore, the main objectives of this work is to evaluate the effect of transesterification process parameters like molar ratio of oil to alcohol, catalyst concentration, and time on the percentage yield of cottonseed oil methyl esters and to find the optimum values of the selected factors using Response Surface Methodology(RSM).

2.0 Materials and Methods

2.1Collection of substrate

Cottonseed oil was purchased commercially from a local firm was used as a substrate. The primary raw materials used in production of biodiesel are cottonseed oil. Cotton seed oil was obtained from seeds of cotton after refining process. These materials contain triglycerides, free fatty acids, and other contaminants.

2.2Reagents collection

Methanol and calcium oxide was purchased from Himedia and Nice chemicals Pvt Ltd. India, for transesterification process. All the reagents used in this work are of scientific grade and can be used straightly without further purification.

2.3Purification of cottonseed oil

Suitable amount of water was taken into a container flask and heated until temperature rises to 70^0C. Suitable amount of cotton seed oil was added into container flask containing hot water, and wait for 30minutes until impure particles settles down. Hot water containing cotton seed oil was collected into the separating funnel and shaked it vigorously for 5 to 10 minutes. Because of low density of cotton seed oil settles on the top of the funnel and high density, water and impurities settled at bottom of the funnel.

Then disperse water and impure particles by opening the funnel valve, after that the purified cotton seed oil was collected into the jar. Collected purified cotton seed oil was heated to 65^0C to remove moisture contained in oil. The purification of cotton seed oil is shown in Figure (1).

Figure 1: Purification process

2.4 Experimental Design

Box-Behnken design was used to develop the experimental runs for cottonseed oil trasesterfication process. A three-level design with three factors was applied, which develpoed 17 experimental runs. This included 6 axial points, 5 central points to give information with respect to the interior of the experimental region and 6 factorial points. Selected transesterfication process parameters for the biodiesel production from cottonseed oil were molar ratio, amount of catalyst (%wt) and extraction time (hrs).The independent variables (coded) levels are shown in Table 1 while Table 2 shows the design matrix of 17 runs with the experimental and predicted yields of methyl ester of cottonseed oil.

Table 1: Input variables and their levels for Box-Behnken design

Independent variable	Units	Range and level		
		-1	0	+1
Molar ratio		5:1	6:1	7:1
Amount of Catalyst	(%wt)	0.3	0.5	0.7
Reaction time	(hrs)	1.5	2.0	2.5

Table 2: Experimental design Matrix by Box-Behnken design

Run	Molar Ratio	Amount of Catalyst (%)	Reaction Time (Hrs)	Theoretical Yield (%)	Predicted Yield (%)
1	5	0.3	2	78.00	78.37
2	6	0.5	2	82.00	82.30
3	7	0.5	2.5	76.00	76.18
4	5	0.7	2	92.00	92.50
5	6	0.5	2	82.00	82.30
6	6	0.5	2	83.50	82.30
7	5	0.5	2.5	87.50	86.81
8	6	0.3	2.5	78.00	78.31

9	6	0.5	2	82.00	82.30
10	6	0.5	2	82.00	82.30
11	7	0.7	2	80.00	79.62
12	6	0.7	1.5	87.50	87.18
13	6	0.3	1.5	76.00	75.81
14	7	0.5	1.5	73.00	73.68
15	6	0.7	2.5	90.00	92.18
16	7	0.3	2	71.00	70.50
17	5	0.5	1.5	84.00	83.81

From Table 2it can be observed that the minimum and maximum values of methyl ester yield were obtained at experimental run numbers of 16 and 4 as 70.50% and 92.50% respectively.

2.5 Transesterification Procedure

Transesterification was carried out in a batch reactor. This reactor consists of the magnetic stirrer with heater, single necked round bottom glass beaker, temperature and stirrer controller. The schematic of experimental setup is shown in Figure (2).

Figure 2: Batch Reactor

A round bottom flask of 1000ml is used for the present analysis. The cotton seed oil in the reactor was heated on a plate having heater and magnetic stirrer arrangement. The mixture was stirred at the constant speed for all test runs. Initially 482ml cotton seed oil is heated to 65^0C. Then the methanol 43ml and the catalyst 0.3gm are mixed. The mixture is transferred to a reactor.

The temperature maintained for the whole transesterification process is about 65^0C, heated up to 2 hours, switched off the apparatus, and waited until the mixture is cooled. The resultant mixture is taken into the separating funnel containing biodiesel and Glycerine. After 3 to 4 hours, glycerine settles down at the bottom of the funnel and Biodiesel settles on the top.

Glycerinis separated by opening the valve of the separating funnel as shown in Figure 3.

Figure 3: Biodiesel Separation

The biodiesel yield of cottonseed oil was determined by the formula given below.

$$\text{Percentage of yield} = \frac{\text{Weight of fatty acid methyl ester}}{\text{Weight of raw cottonseed oil used}} \times 100\% \qquad (1)$$

2.6 Statistical Data Analysis

The data obtained from the transesterification experiments were analyzed statistically using RSM, to fit the quadratic polynomial equation developed by the Design-Expert software trail version 10.0.3.1 (Stat-Ease Inc., Minneapolis, USA). The fitted polynomial equation is shown in Equation (2).

$$R = \beta_0 \pm \sum_{i-1}^{n} \beta_i X_i \pm \sum_{i=1}^{n} \beta_{ii} X_i^2 \pm \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \qquad (2)$$

Where,

R = the response (percentage of biodiesel yield)
β_0 = constant,
β_i =regression coefficient of the linear terms,

β_{ii} = regression coefficient of the quadratic terms,
β_{ij} = regression coefficient of interaction terms,
$X_i X_j$ = coded variables,
n=number of independent variables

3.0 Results and Discussion

3.1 Model Fitting and Summary Statistics

As discussed in previous section, for optimization of transesterfication process of cottonseed oil, three process parameters were investigated namely; molar ration, amount of catalyst and conversion time. The statistical summary of the cottonseed oil transesterification using Box-Behnken design has been shown in Table 3.

Table 3: Model Summary Statistics

Source	Std.Dev	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	1.64	0.9351	0.9201	0.8740	67.46	
2FI	1.68	0.9470	0.9152	0.7688	123.80	
Quadratic	0.74	0.9928	0.9835	0.9331	35.81	Suggested
Cubic	0.67	0.9966	0.9866		+	Aliased

The highest order polynomial was selected from the model summary statistics, where the model is not aliased and additional terms are significant. The predicted R-squared of 0.9331 is in reasonable concurrence with the adjusted R-Squared value of 0.9835. The resulted quadratic model in terms of coded factors is as follows:

$$R = +82.30 - 5.19A + 5.81B + 1.38C - 1.25AB - 0.13AC + 0.12BC - 2.40A^2 + 0.35B^2 + 0.22C^2 \qquad (3)$$

The Equation (3) in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1.The coded equation is helpful for determining the relative impact of the factors by considering the factor coefficients. While the final model equation in terms of actual factors is given by the Equation (4)

$$\begin{aligned} Percentage\ of\ Yield &= -7.71875 + 27.23750X\ Molar\ ratio + 55.31250X\ Amount\ of\ Catalyst \\ &+0.025000X\ Amount\ of\ Catalyst - 6.25000X\ Molar\ ratioX\ Amount\ of\ Catalyst \\ &-6.25000X\ Molar\ ratioXAmount\ of\ Catalyst - 0.25000X\ Molar\ ratioXReaction\ Time \\ &+1.25000X\ Amount\ of\ CatalystXReaction\ Time - 2.40000X\ Molar\ ratio^2 \\ &+8.75000X\ Amount\ of\ Catalyst^2 + 0.90000X\ Reaction\ Time^2 \end{aligned} \quad (4)$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

3.2 Analysis of Variance (ANOVA)

Design Expert Software trail Version 10.0.3.1 was used to develop a quadratic model. Further, summary of Analysis of variance (ANOVA) technique was used to evaluate how good the model fits, see Table (4).

Table 4: 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	531.58	9	59.06	107.04	< 0.0001	significant
A-Molar ratio	215.28	1	215.28	390.15	< 0.0001	
B- Amount of Catalyst	270.28	1	270.28	489.83	< 0.0001	
C-Reaction Time	15.13	1	15.13	27.41	0.0012	
AB	6.25	1	6.25	11.33	0.0120	
AC	0.063	1	0.063	0.11	0.7463	
BC	0.063	1	0.063	0.11	0.7463	
A^2	24.25	1	24.25	43.95	0.0003	
B^2	0.52	1	0.52	0.93	0.3658	
C^2	0.21	1	0.21	0.39	0.5539	
Residual	3.86	7	0.55			
Lack of Fit	2.06	3	0.69	1.53	0.3370	Not significant
Pure Error	1.80	4	0.45			
Cor Total	535.44	16				

From Table (4), it may be observed that the model F-value of 107.04 suggests the model is significant. Values of prob> F less than 0.0500 indicate model terms are important. For the current quadratic model, the values of probability F are less than 0.0500 for factors A, B, C, AB, and A^2 that express the model terms are significant. It is also worth noting that the factors A and B mainly affect the response. Moreover, the lack of fit F-value of 1.53 implies the lack of fit is not significant relative to the pure error.

3.3 Model Diagnostic Plot

The predicted values of response were plotted against the actual response values, which were obtained from experimentations, see Figure 4. It can be deduced that the diagnostic plot, i.e. Figure 4, indicates a linear relationship between the actual and predicted values that shows the adequacy of the proposed model.

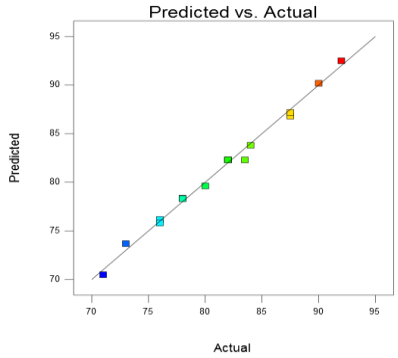


Figure 4: Predicted and Actual values of response

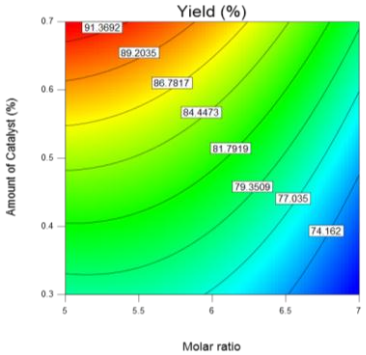
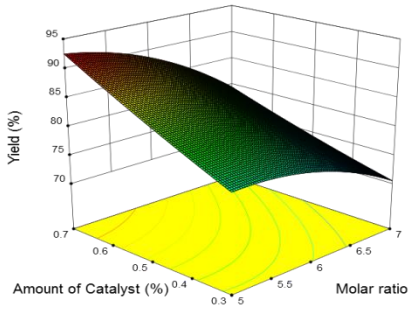


Figure 5: (a) Contour plot



(b) 3 D surface plot of response with respect to molar ratio and amount of catalyst

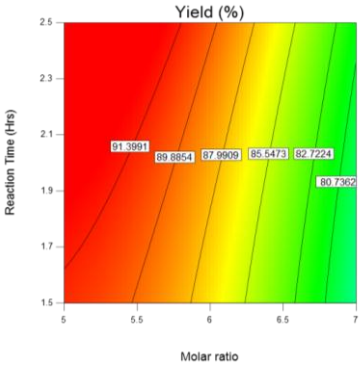
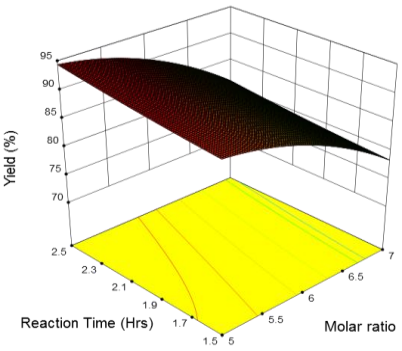


Figure 6: (a) Contour plot



(b) 3 D surface plot of response with respect to molar ratio and reaction time

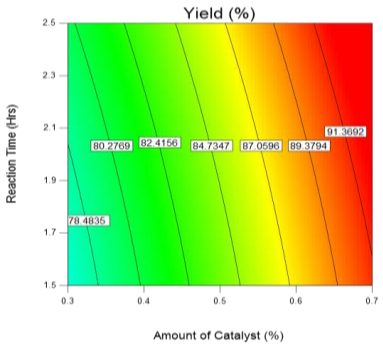
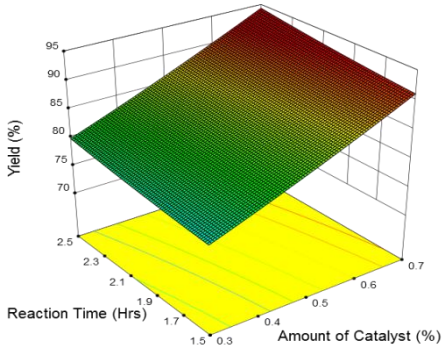


Figure 7 :(a) Contour plot



(b) 3 D surface plot of response with respect to reaction time and amount of catalyst

3.4 Response Surface Plots

The contour and 3D response surface plots of the proposed model have been shown in Figure 5 to Figure 7 that represents the analysis of interaction effects of the preferred variables.

The contour plots Figure 5a, and 3D surface plot of response, Figure 5b, indicates the effect of interaction of molar ratio and catalyst concentration on percentage of yield of cottonseed oil methyl ester, while reaction temperature and reaction time were fixed at 65^0C and 2 h, respectively. From the plot, it was observed that the percentage yield of methyl ester increased with the increase in catalyst concentration. Moreover, it was found that the decrease in molar ratio provides higher methyl ester yield.

The contour plots Figure 6a, and 3D surface plot of response, Figure 6b, indicates the effect of interaction of molar ratio and reaction time on percentage of yield of methyl ester.

From plots, it was deduced that increase in reaction time at constant molar ratio and constant catalyst helped the reaction to produce more yield. Reaction time has the linear characteristics with molar ratio. More reaction time allowed the transterification reaction to utilize the excess methanol and catalyst. Even though the molar ratio have the negative impact on methyl ester production but increased in reaction time helped the reaction to complete. Lowering the reaction time and increasing the molar ratio caused more glycerol formation.

The contour plots Figure 7a, and 3D surface plot of response, Figure 7b, indicates the effect of interaction of reaction time and catalyst concentration on percentage of yield of cottonseed oil methyl ester. From figures, it was found that catalyst and reaction time has similar characteristic behavior with molar ratio. Higher reaction time allowed the proper utilization of catalyst in transterification process. Transterification process up to 2 hr is helped to produce higher yield, but the transterification process is reversible increase in reaction time leads to reduction in yield.

The optimum values of molar ratio, amount of catalyst and reaction time have been found as 5:1, 0.7(%wt), and 2hrs respectively, when predicted oil recovery is 92.37%.The confirmatory experimental run was performed at optimum values of variables and was verified.

4.0 Conclusion

In this work, the parametric optimization of trasesterfication of cottonseed oil was performed. The process parameters, like molar ratio (A), amount of catalyst (B) and reaction time (C) were optimized using RSM under Box-Behnken design. For optimization, a quadratic model was developed and validated. Analysis of Variance (ANOVA) was performed, which indicates that the three linear terms has the more significant effect on percentage of yield, further one cross product term (AB) and one quadratic term (A^2) were found significant. The maximum cottonseed oil methyl ester yield of 92.37% was determined when molar ratio, catalyst concentration and reaction time, were 5:1, 0.7 (%wt) and 2 hrsrespectively. Finally it was concluded that the process parameter optimization using RSM under Box-Behnken design provides better cottonseed oil methyl ester yields.

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