Research Article

Optimization of Alkali Catalyzed Transesterification of Safflower Oil for Production of Biodiesel

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The Central Composite Design is used for the optimization of alkaline catalyzed transesterification parameters such as methanol quantity, catalytic concentration, and rotational speed by keeping the temperature and reaction time constant. The Central Composite Design method is employed to get the maximum safflower oil methyl ester yield. The combined effects of catalyst concentration, rotational speed, and molar ratio of alcohol to oil were investigated and optimized using response surface methodology. A statistical model has predicted the maximum yield of safflower oil methyl ester (94.69% volume of oil) parameters such as catalyst concentration (0.6 grams), methanol amount (30 mL), rotational speed (600 rpm), and keeping constant reaction temperature (55°C to 65°C) and reaction time (60 minutes). Experimental maximum yield of 91.66% was obtained at above parameters. XLSTAT is used to generate a linear model to predict the methyl ester yield as a function of methanol quantity, catalyst concentration, and rotational speed by keeping constant reaction temperature (55°C to 65°C) and reaction time (60 minutes). MINITAB is used to draw the 3D response surface plot and 2D contour plot to predict the maximum biodiesel yield.

1. Introduction

Energy consumption is the basic requirements for human existence. Fossil fuels are the main suppliers of energy for today's world. Due to increasing global warming and consumption of fossil fuels leading to huge petroleum crisis, hence there is a need to find out the alternative renewable energy sources for fuel generation [1, 2]. Oil crisis during 1971 in the world is also the notable reason for finding the alternative sources for the conventional oils. The highest percentage of total energy output in the world is obtained from fossil fuels and they are finite resources. 79% of the Indian crude oil requirement is met by imports. It is reported that India has consumed 73500 million tons of diesel oil and 16335 million tons of petrol for the year 2013-14. The values of petroleum products imported during 1913-1914 were 16.718 million metric tons (MMT) valued at Rs 74,605 crore and during 2012-2013 petroleum products were 15.774 MMT valued at Rs 68363 crore. Imports of petroleum products increased

by 5.98% in terms of quantity and increased by 9.13% in terms of values. The cost of the conventional diesel oil fluctuates day by day and it affects the economies of oil importing countries [3]. So, by using conventional diesel oil that leads to the formation of high HC, NO_x, CO, and particulate matter it has greater effect on environmental changes causing the severe problems on human beings. Use of conventional diesel oil increases the global warming, greenhouse effect, unseasonable rains, and acid rain formation [4–6]. The most practical way to reach this demand is by using alternative fuels. The alternative energy or fuel is renewable energy sources and it is free energy sources that have no undesirable consequences on the environment [7, 8]. Among the various alternative energy sources, biodiesel exhibits a great potential. The term biodiesel commonly refers to oxygenated diesel fuel and it is made from various renewable feed stocks by the conversion of the triglycerides to respective esters. Biodiesel consists of long chain fatty acids of monoalkyl esters of nontoxic, biodegradable, and sulphur-free renewable energy

and it is obtained from the conversion of triglycerides to esters by transesterification with alcohol in the presence of acid or base catalyst.

The transesterification process is a very important process in the production of biodiesel because it reduces the viscosity of vegetable oils and brings it nearer to that of conventional diesel oil, thus avoiding the engine related problems and increasing the engine life. Alkali catalyzed transesterification reaction is the most adopting methods for production of biodiesel because it is simple to extract the respective esters. This process is only applicable for oils that have low free fatty acid level (<4) and acid catalyst transesterification process is applicable only for high free fatty acid level (>4) oils.

Enzymatic catalyzed transesterification can also be used for the production of biodiesel from low grade feedstock like used cooking oil, animal fat, and so forth. This process is carried out in the presence of enzyme such as lipase. This process has many advantages over the conventional transesterification process like generation of zero byproduct, no difficulty in separation, and requiring moderate reaction conditions. However, yield, reaction times, and costs are still critical compared to alkaline catalyzed transesterification reaction [9, 10].

Noncatalyzed Biox transesterification process is a new method available for the production of biodiesel. In transesterification reaction biodiesel yield is slow because of the low solubility of alcohol in oil. This problem is solved by using a cosolvent, tetrahydrofuran, to stabilize methanol [11, 12].

Noncatalyzed supercritical methanol method is the most recent method available for producing biodiesel. This method requires only 4 minutes to complete the reaction but requires high alcohol-oil ratio, high capital cost, and high pressure (80 bar) and temperature (350°C–400°C) [13–15].

In this present study, experiments have been carried out according to Central Composite Design (CCD) to understand the relation between the process variables and biodiesel yield by using alkaline base-catalyzed transesterification process. A CCD method was used to find out the optimal experimental conditions for production of biodiesel. CCD has the advantage of predicting response or yield based on a few sets of experimental results in which all the parameters varied within the range.

2. Materials and Methods

2.1. Materials. Unrefined low grade safflower oil is kindly supplied by the supplier and methanol was used as reactants and NaOH was used as catalyst for the transesterification process.

2.2. Methods. Free fatty acid level was found out by using the titration method and it was found to be less than 4%. The alkaline stage transesterification process was used for the production of biodiesel. Sodium hydroxide is used as an alkaline catalyst transesterification process because it is cheaper and reacts faster than acid catalyst.

FIGURE 1: Magnetic stirrer with hot plate.

2.2.1. Transesterification. The low grade safflower oil was converted into methyl esters through alkaline base-catalyzed transesterification process with methanol in the presence of NaOH catalyst. Before the transesterification process, the dust particle and other impurities have been removed from the low grade safflower oil by filtration with cloth filter. After that process, take the required quantity of low grade safflower oil and add required amount of methanol and NaOH to 1000 mL beaker placed on a magnetic stirrer having hot plate (Figure 1) with continuous heating and rotational system. The thermometer is placed inside the beaker such that it is just in contact with the surface of the oil. This mixture was stirred and heated to 60°C for 1 hour and then allowed to cool to attain room temperature for 8 to 10 hours [16]. Then the biodiesel and glycerol layers separated in separating funnel. Finally, methyl esters of low grade safflower oil were purified with normal water and heating to 90°C by using a magnetic stirrer with hot plate.

2.2.2. Experimental Design

(1) Parameter Design Methodology. In order to optimize the transesterification process parameters a five-level-three-factor CCD has been used. Three control parameters such as methanol (D) in mL, sodium hydroxide (E) in grams, and rotational speed (F) in RPM have been selected for optimization of biodiesel yield. Each of the three control parameters has been treated at five levels. Table 1 shows the code and uncoded levels of independent variables.

(2) Design of Experiments. Table 2 shows that the experimental matrix for CCD and biodiesel yield for alkaline catalyzed transesterification process. Twenty experiments have been conducted by keeping constant reaction temperature (55°C to 60°C) and reaction time (60 minutes).

2.3. Experimental Procedure. Sample (Figure 2) has been taken into the beaker and it is maintained at the constant

TABLE 1: Independent parameter and levels used in CCD.

Parameters	Levels				
	−1.68 (−α)	−1	0	1	+1.68 (+α)
CH$_3$OH in mL (D)	16.6	20	25	30	33.4
NaOH concentration (E) in grams	0.464	0.6	0.8	1.0	1.136
Rotational speed in RPM (F)	332	400	500	600	768

temperature (55°C to 60°C) and reaction time (60 minutes). The sodium methoxide solution was prepared by dissolving the required amount of NaOH in a certain amount of methanol. Half of prepared sodium methoxide is added to the sample and continues rotational speed and heating with a magnetic stirrer having a hot plate (Figure 1) for 10 to 15 minutes. Then add remaining half of the prepared sodium methoxide solution into the sample for 45 to 50 minutes with continuous rotational speed and heating. A similar procedure is carried out for 20 experiments which have been conducted as per the experimental matrix shown in Table 2. On completion of reaction, the mixture is allowed to cool to room temperature and it is falling into two layers. Top one layer is crude safflower oil methyl ester and bottom one is crude glycerin. Figures 3, 4, and 5 show optimized samples which were obtained as per Table 2. The crude safflower oil methyl ester was washed twice with water to bring the pH to 7.

2.4. Statistical Analysis. The experimental data have been analyzed with XLSTAT for quadratic least square technique procedure using (1). In this work, XLSTAT for quadratic least square technique with MINITAB software have been used in the regression analysis and analysis of variance (ANOVA) and to generate surface plots using the fitted quadratic polynomial equation obtained from regression analysis (2). Few experiments have been conducted to validate the equation using a combination of the independent variables. Selected variables are within the experimental range

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{j=1}^{n} \beta_j X_j + \sum_{k=1}^{n} \beta_k X_k + \sum_{i}^{n} \sum_{j}^{n} \beta_{ij} X_i X_j$$
$$+ \sum_{i}^{n} \sum_{k}^{n} \beta_0 X_i X_k + \sum_{j}^{n} \sum_{k}^{n} \beta_0 X_j X_k + \sum_{i=1}^{n} \beta_{ii} X_i^2 \qquad (1)$$
$$+ \sum_{j=1}^{n} \beta_{jj} X_j^2 + \sum_{k=1}^{n} \beta_{kk} X_k^2,$$

where Y is the response variable; X_i, X_j, and X_k are coded independent variables; β_0, β_i, β_{ii}, β_{ij} and β_{ik} are the intercept, linear, quadratic, and interaction constant coefficients, respectively; and n is the number of factors studied and it optimized in the experiment. The regression model has been found to be highly significant with the correction coefficients (Table 3) of determination of R^2 having a value of 0.909. The predicted model for a percentage of safflower oil methyl esters

FIGURE 2: Sample for test.

FIGURE 3: Optimized samples 1–6.

yield in terms of coded factors has been given in the following [17, 18]:

$$Y = 86.27 + 2.80 * X_1 - 8.54 * X_2 - 2.72 * X_3 - 0.52$$
$$* X_1^2 - 5.20 * X_2^2 + 0.67 * X_3^2 + 1.90 * X_1 \qquad (2)$$
$$* X_2 + 3.26 * X_1 * X_3 - 3.47 * X_2 * X_3.$$

A statistical model (2) predicted that the maximum safflower oil methyl ester (94.694) yield has been obtained at the optimized methanol quantity (30), catalyst (0.6), and rotational speed (600). Experimentally, yield (91.66) has been obtained at the above parameters. Extracting the biodiesel of safflower oil by utilizing these values in mass production has been shown (Plate 3.8 and Plate 3.9).

3. Result and Discussion

3.1. Effect of Methanol and NaOH on Experimental Yield. Figure 6 shows the 3D response surface and 2D contour plot between methanol quantity and concentration of NaOH for different fixed parameter. From Figure 6 it can be seen that yield (%) increases with the increase in the quantity of methanol in concentration of NaOH. This has reached the maximum yield 91.66% of safflower oil methyl ester at 0.6-gram concentration of NaOH and 30 mL of methanol. Then the yield is decreased by an increase in the concentration of NaOH in quantity of methanol. This has reached the 59.82% of safflower oil methyl ester yield by increase to 1-gram concentration of NaOH and 20 mL of methanol quantity.

This is due to the fact that there is less significant interaction between quantity of methanol and concentration of NaOH and negative concentration of the quadratic coefficient mostly caused by soap formation side reaction, resulting in a decrease in yield.

3.2. Effect of Methanol and Rotational Speed on Experimental Yield. Figure 7 shows the 3D response surface and 2D

TABLE 2: Experimental matrix for CCD and results.

Exp. number	D	E	F	CH$_3$OH (mL)	NaOH (grams)	Rotational speed (RPM)	Yield (%)	
							Experimental	Predicted
1	−1	−1	−1	20	0.6	400	91.07	91.390
2	−1	−1	1	20	0.6	600	83.63	86.362
3	−1	1	−1	20	1.0	400	82.60	77.425
4	−1	1	1	20	1.0	600	59.82	58.518
5	1	−1	−1	30	0.6	400	87.50	86.661
6	1	−1	1	**30**	**0.6**	**600**	**91.66**	**94.694**
7	1	1	−1	30	1.0	400	85.18	80.307
8	1	1	1	30	1.0	600	76.92	74.459
9	0	0	−1.68	25	0.8	332	87.50	92.751
10	0	0	1.68	25	0.8	668	85.83	83.607
11	0	−1.68	0	25	0.464	500	90.93	85.938
12	0	1.68	0	25	1.136	500	50.00	57.180
13	−1.68	0	0	16.6	0.8	500	79.09	80.094
14	1.68	0	0	33.4	0.8	500	87.50	89.523
15	0	0	0	25	0.8	500	86.36	86.273
16	0	0	0	25	0.8	500	86.36	86.273
17	0	0	0	25	0.8	500	86.36	86.273
18	0	0	0	25	0.8	500	86.36	86.273
19	0	0	0	25	0.8	500	86.36	86.273
20	0	0	0	25	0.8	500	86.36	86.273

TABLE 3: Regression coefficient of predicted quadratic polynomial model.

Terms	Coefficients	Standard errors	Computed t-value	P value
Linear				
β_0	86.27	1.74	49.56	0.000
β_1	2.80	1.16	2.43	0.036
β_2	−8.55	1.16	−7.40	0.000
β_3	−2.72	1.16	−2.35	0.040
Quadratic				
β_{11}	−0.52	1.12	−0.46	0.655
β_{22}	−5.20	1.12	−4.63	0.001
β_{33}	0.67	1.12	0.60	0.562
Interaction				
β_{12}	1.90	1.51	1.26	0.236
β_{13}	3.26	1.51	2.16	0.056
β_{23}	−3.47	1.51	−2.30	0.044
R^2	0.909			

FIGURE 4: Optimized samples 7–10.

FIGURE 5: Optimized samples 11–15.

contour plot between quantity of methanol and rotational speed for different fixed parameter. From Figure 7 it can be seen that yield (%) increases with the increase in the quantity of methanol and rotational speed. This has reached the maximum methyl ester yield of 91.66% at 30 mL of methanol and 600 rpm of rotational speed. Then the yield is decreased by a decrease in quantity of methanol and the increase in the rotational speed. This has reached the 59.82% of safflower oil

methyl ester yield by an increase to 600 rpm rotational speed and 20 mL methanol to oil. This is due to the fact that there is less significant interaction between quantity of methanol and rotational speed and negative concentration of the quadratic coefficient mostly caused by soap formation side reaction.

If vegetable oil contains free fatty acid, it will react with homogenous base catalysts to form soap and water. The sodium soaps are soluble in the glycerol phase and must be isolated after neutralization by decantation as fatty acids. The loss of esters converted to fatty acids can reach as high as 1% of the biodiesel production.
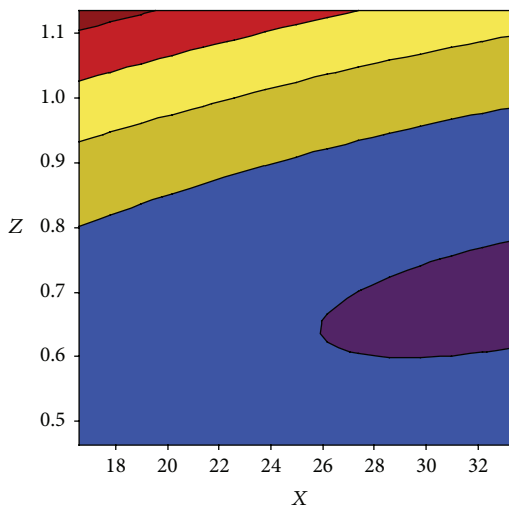
3.3. Effect of NaOH and Rotational Speed on Experimental Yield. Figure 8 shows the 3D response surface and 2D contour plot between the concentration of NaOH and rotational
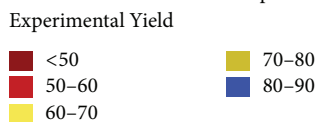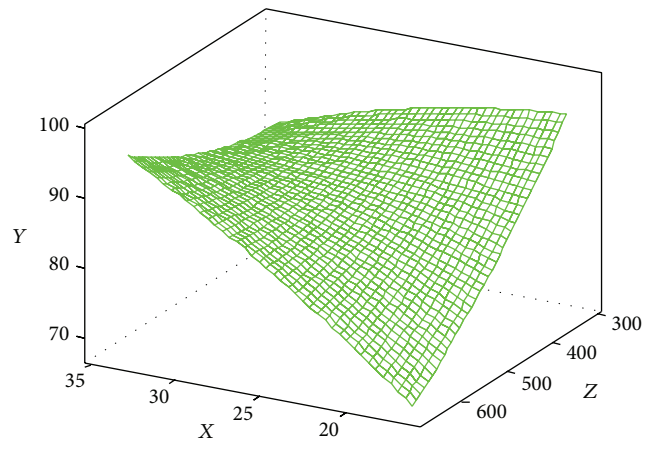
3D response surface plot

(a)

2D contour plot
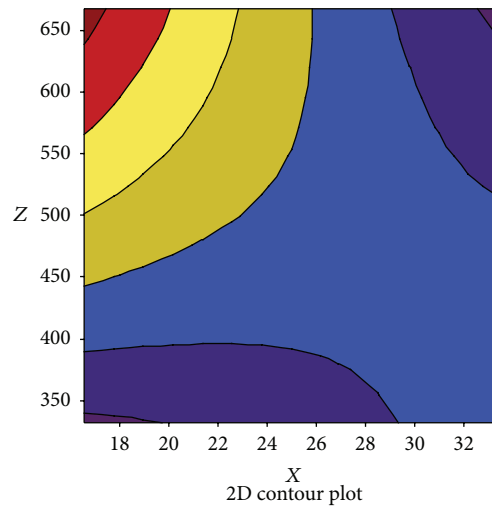
Experimental Yield

■	<50	■	70–80
■	50–60	■	80–90
■	60–70		
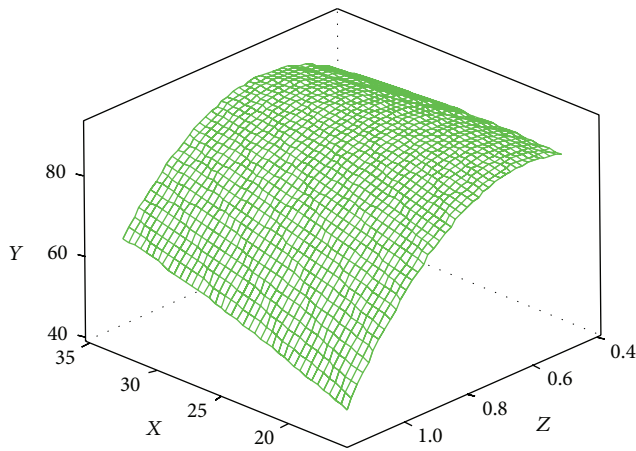
(b)

FIGURE 6: Effect of methanol (X) and NaOH (Z) on Experimental Yield (Y).

3D response surface plot

(a)

2D contour plot

Experimental Yield

■	<70	■	85–90
■	70–75	■	90–95
■	75–80	■	>95
■	80–85		

(b)

FIGURE 7: Effect of methanol (X) and rotational speed (Z) on Experimental Yield (Y).

speed for different fixed parameter. From Figure 8 it can be seen that yield (%) increases within the rotational speed to the concentration of NaOH. This has reached the maximum safflower oil methyl ester yield 91.66% at 0.6-gram concentration of NaOH and 600 rpm of rotational speed. Then the yield is decreased by an increase in the concentration of NaOH and increase in the rotational speed. This has reached 59.82% of safflower oil methyl ester yield by increasing to 600 rpm rotational speed and 1-gram concentration of NaOH. This is due to the fact that there is less significant interaction between the concentration of NaOH and rotational speed and negative
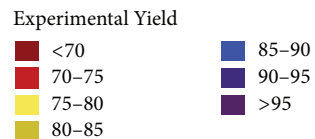
concentration of the quadratic coefficient mostly caused by soap formation side reaction.

4. Conclusion

In this present study, experiments have been carried out according to CCD to understand the relation between the process variables and biodiesel yield. CCD method was used to find out the optimal experimental conditions for maximum biodiesel yield. CCD has the advantage of predicting yield based on a few sets of experimental results in which all the parameters varied within the range. A statistical model has predicted the maximum yield of safflower oil methyl ester
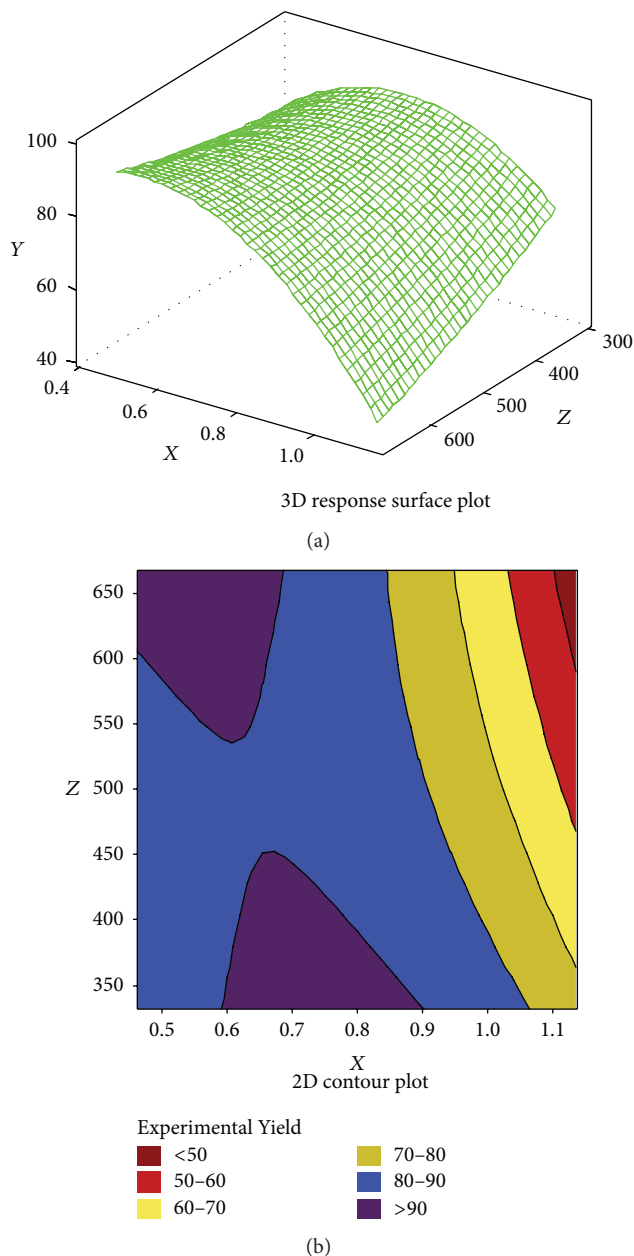
3D response surface plot

(a)

X

2D contour plot

(b)

Experimental Yield

■ <50	■ 70–80
■ 50–60	■ 80–90
■ 60–70	■ >90

FIGURE 8: Effect of NaOH (X) and rotational speed (Z) on Experimental Yield (Y).

(94.694% volume of oil) parameters such as catalyst concentration (0.6 grams), methanol amount (30 mL), rotational speed (600 rpm), and keeping constant reaction temperature (55°C to 65°C) and reaction time (60 minutes). Experimental maximum yield of 91.66% was obtained at above parameters.

Conflict of Interests

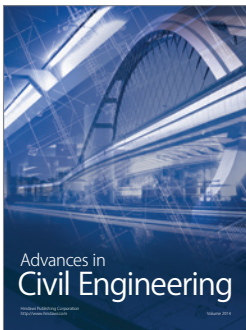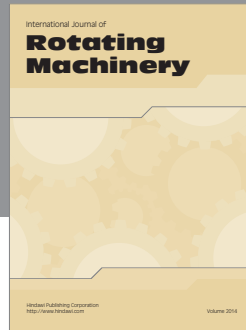The authors declare that there is no conflict of interests regarding the publication of this paper.

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