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FULL LENGTH ARTICLE

Optimization of biodiesel production from refined cotton seed oil and its characterization

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Response surface
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Optimization

Abstract Biodiesel was produced through transesterification of refined cotton seed oil with methanol and potassium hydroxide (KOH) as a catalyst using batch mode. The physicochemical properties of cotton seed oil and biodiesel as an alternative fuel for diesel engine was characterized through ASTM standards for fuel tests. The functional groups of the biodiesel were investigated using Fourier transform infrared spectroscopy. Influence of key parameters like reaction temperature, reaction time, catalyst concentration and methanol/oil molar ratio were determined using batch mode. These process parameters were optimized using response surface methodology (RSM) and analysis of variance (ANOVA). The significance of the different process parameters and their combined effects on the transesterification efficiency were established through a full factorial central composite design. The results obtained are in good agreement with published data for other vegetable oil biodiesel as well as various international standards for biodiesel fuel. An optimum yield of 96% was achieved with optimal conditions of methanol/oil molar ratio, 6:1; temperature, 55 °C; time, 60 min; and catalyst concentration, 0.6%. This investigation has shown that cotton seed oil from Nigeria can be used to produce biodiesel.

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1. Introduction

In the past the world energy demand has relied on non-renewable fossil fuels for energy generation, transportation and industrial applications. The gaseous emissions from the combustion of these fuels are the principal causes of global warming and many environmental consequences.

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The depletion of world crude oil reserves and increased deteriorating climate conditions associated to the use of fossil fuels have stimulated the search for an alternative and efficient fuel by many researchers in recent years. One of the most promising alternative fuels is biodiesel, which has attracted attention worldwide [1]. This is due to its overwhelming benefits over the conventional petro diesel. It is renewable, biodegradable, and non-toxic, with high flash point and good reduction in greenhouse emissions profile [2,3].

Biodiesel is the free fatty acid methyl esters known as FAME, derived from fat and oil sources. There are various

processes that have been adopted in the production of biodiesel from vegetable oils and animal fats among which transesterification is the key and foremost important process to produce the cleaner and environmentally safe fuel [4,5].

The transesterification is usually carried out using primary and secondary alcohols. Fukuda et al. [6] reported that methanol and ethanol are most frequently used in the production of biodiesel but methanol is more preferred due to its low cost. Biodiesel has been produced through transesterification of edible oils [1]. Presently, more than 95% of commercial biodiesel is produced from edible oil, such as cotton seed, rapeseed, palm, sunflower and soybean oil [3].

There are several parameters that affect the yield of biodiesel through transesterification of vegetable oils. They are alcohol/oil molar ratio, catalyst concentration, reaction temperature, reaction time and agitation speed. The optimization of transesterification reaction requires a large number of experiments and mathematical tool that can predict the effect of each process parameter of the reaction and their interactions. Response surface methodology has been successfully applied to the optimization of biodiesel production from different raw materials and different types of catalysts.

In this study, response surface methodology in combination with central composite design was applied to optimize the transesterification of refined cottonseed oil with methanol in the presence of potassium hydroxide to produce biodiesel.

2. Materials and methods

2.1. Materials

Refined cotton seed oil was obtained from Shoprite Enugu, reagents from Head Bridge Onitsha and petro diesel was obtained from Total filling station Awka, Anambra State, Nigeria.

2.2. Methods

A precise quantity of the oil was measured and poured into a conical flask. The oil was pre-heated to 50 °C (using water bath with temperature regulator). A specific amount of potassium hydroxide pellets was weighed and dissolved in the required amount of methanol. The potassium methoxide solution was then added to the pre-heated oil in a 250 ml three-neck glass flask and placed on a hot plate magnetic stirrer at a particular temperature with a constant speed of 300 rpm. The reaction was allowed to stand for a defined time and then stopped. The product of the reaction was kept overnight for proper settling of the biodiesel produced. The product was separated from glycerol using separating funnel.

Then, 50 ml of water was measured and poured gently on the product sample to purify it. The mixture was gently stirred to avoid foam formation and was left overnight to settle into two phases namely; water-impurity phase and biodiesel phase. The two phase mixture was separated using separating funnel. The biodiesel layer was then heated to 100 °C for 1 h to evaporate the remaining water molecules in it. The percentage of the biodiesel yield was determined by comparing the weight of layer biodiesel with the weight of refined cottonseed oil used.

$$\text{Biodiesel Yield(\%)} = \frac{\text{weight of fatty acid methylester}}{\text{weight of oil used}} \times 100\% \quad (1)$$

2.3. Physiochemical characterization of oil and biodiesel produced

The physiochemical properties of the oil and the biodiesel were characterized according to ASTM D6751-02 [7] and Nigeria standards as described by Mohammed et al. [8].

2.3.1. Determination of the moisture content

About 1 g each of oil and biodiesel were weighed out in pre-weighed petri dishes. The two samples were placed in an oven and dried at 100 °C for 2 h. The weights of the samples were taken every 30 min. The procedure was repeated until a constant weight was obtained. After each 30 min, each sample was removed from the oven and kept in a desiccator to cool, and was reweighed. The cooled dishes each were weighed and the result of each dry sample was determined and recorded.

The percentage moisture in the samples was calculated from the formula:

$$\text{Percentage moisture content} = \frac{W_1 - W_2}{W_1} \times \frac{100}{1} \quad (2)$$

where, W_1 = original weight of the sample before drying, W_2 = weight of the sample after drying.

2.3.2. Determination of saponification value

1 g of each sample (oil and biodiesel) was dissolved in 25 ml of 0.5 M ethanolic potassium hydroxide solution, using 250 ml quick fit flask. The flask was heated in a steam bath under reflux for 30 min with occasional swirling. The resultant solution was heated with 0.5 M HCl using phenolphthalein indicator. A blank determination was carried out under similar conditions.

The difference in the above two titre values gives the number in milli-litres of HCl acid required to neutralize the alkali after saponification.

The saponification value was carried out as follows:

$$\text{Saponification value, SV(mg KOH)} = \frac{56.1 \times M \times (B - V)}{W} \quad (3)$$

Where, M is the morality of standard HCl (0.5 M), B is the volume of HCl in ml used in the blank titration, V is the volume of HCl in ml used for oil and biodiesel titration respectively, 56.1 is the molar mass of potassium hydroxide, and W is the weight in gram of the oil sample.

2.3.3. Determination of iodine value

1 g of each sample was dissolved in 15 ml of carbon tetrachloride. The solution was mixed with 25 ml Wiji's solution. The flask with the content was stoppered and allowed to stand in the dark for thirty minutes at room temperature, to enable oxidation to take place. Then 100 ml of distilled water and 20 ml of 10% potassium iodide solution were added to the content of the flask. The resultant mixture was titrated with 0.1 M sodium

thiosulphate using 10% starch solution (weight by volume). A blank determination was carried out in the same manner under similar conditions.

The iodine value was calculated thus:

$$\text{Iodine value, } IV(\text{gI}_2/100 \text{ g oil}) = \frac{12.69 \times M(B - V)}{W} \quad (4)$$

where, M is the molarity/strength of standard thiosulphate solution, B is the volume of $\text{Na}_2\text{S}_2\text{O}_4$ in ml used in the blank titration, V is the volume of $\text{Na}_2\text{S}_2\text{O}_4$ in ml used in test titration, and W is the weight in gram of the oil sample.

2.3.4. Determination of acid value

1 g of each sample was dissolved in a 25 ml neutral mixture of solvent (equal volume of diethyl ether and absolute ethanol). The resultant oil solution was titrated with 0.1 M potassium hydroxide (KOH) solution, using phenolphthalein indicator. The titration continued, until a pink coloured solution was obtained, indicating the end point.

The acid value was calculated using the expression below:

$$\text{Acid value}(\text{mg KOH/g}) = \frac{5.61 \times M \times V}{W} \quad (5)$$

M is the molarity of standard KOH (0.1 M), V is the volume of KOH in ml, 56.1 is the molar mass of potassium hydroxide. W is the weight in gram of the oil sample.

2.3.5. Determination of free fatty acid (FFA)

1 g each of oil and biodiesel samples was dissolved in a 25 ml neutral mixture (equal volume of diethyl ether and absolute ethanol). The resultant oil solution was titrated with 0.1 M potassium hydroxide solution with a phenolphthalein indicator added in 3 drops. The titration continued until the end point was reached. The end point was recorded as the appearance of a permanent pink colour.

The free fatty acid was expressed in terms of oleic acid and computed using the expression below:

$$\text{FFA}(\%) = \frac{TV \times 0.0282 \times 100}{W} \quad (6)$$

Where, TV is the titre value $0.0282 = \text{constant}$ (weight of oleic acid neutralized by 1 mg of KOH). $W =$ the weight in gram of the oil sample.

2.3.6. Determination of ester value

The ester value of the oil and biodiesel samples was calculated as the difference between the saponification value and the acid value. Therefore,

$$\text{Ester value} = \text{Saponification value} - \text{Acid value} \quad (7)$$

2.3.7. Determination of the peroxide value

1 g each of oil and biodiesel was added to a clean dry boiling tube containing 1 g of powdered potassium iodide and 20 ml of solvent mixture (2 vol glacial acetic acid + 1 vol of chloroform). CO_2 was gently bubbled through the mixture of each sample and solvent. The tube was placed in boiling water and boiled vigorously for 30 s. Each of the contents was quickly poured into a flask containing 20 ml of 5% potassium iodide solution and the tubes were washed out twice with 10 ml

of water then titrated with 0.002 M sodium thiosulphate solution using starch indicator. The titration continued until the yellow colour disappeared. A blank determination (without oil or biodiesel) was carried out at the same time and condition. The peroxide value was calculated by the expression below:

$$\begin{aligned} \text{Peroxide value, PV}(\text{mili equivalents}/100 \text{ g sample}) \\ = \frac{1000 \times N \times (V - B)}{W} \end{aligned} \quad (8)$$

where, $N =$ the normality of sodium thiosulphate solution, $B =$ the titration of blank in ml, $V =$ the titration of test sample in ml, $W =$ the weight of the oil, 1000 is the standard factor for peroxide value.

2.3.8. Determination of specific gravity

A 25 ml specific gravity bottle was weighed while empty. The bottle was filled with water and reweighed. After draining the bottle the oil and biodiesel sample each was poured into the bottles and the weights recorded. The experiment was carried out as quickly as possible at the same temperature (room temperature). The specific gravity of the oil sample (i.e. cotton seed oil) was calculated respectively from the recorded weight using the relation;

$$\text{Specific gravity, S.G.} = \frac{\text{weight of sample}}{\text{weight of equal vol. of water}} \quad (9)$$

2.3.9. Determination of viscosity

The rheological behaviour was tested by means of the absolute viscosity determined in a Brookfield viscometer LV –DVII model, at varying temperatures using spindle 62. The temperature of the samples was raised to various temperatures with constant temperature magnetic hot plate. The viscosity measurements were then taken at different shear rates.

2.3.10. Determination of refractive index

A few drops of oil and biodiesel sample were put on the glass slide of the refractometer. Water 30°C was circulated round the glass slide to keep its temperature uniform. A little fluorescence tube was brought near the apparatus at the glass slide and observed through aperture, (i.e. the eye piece of the refractometer). The centre of the circle was adjusted (taken down) to where it corresponds to the graduated scale pointed to the refractive index. Hence the refractive indexes of the oil and biodiesel sample were determined.

2.3.11. Boiling point determination

20 ml of biodiesel was poured into a heating beaker and thermometer inserted, carefully converted and heated with a hot plate. As the temperature increases, the point at which the sample started boiling, was recorded.

2.3.12. Cloud point and pour point determination

A cooling bath containing a freezing mixture of salt and water to obtain a lower range of temperature was used. 50 ml of methyl ester and oil were placed in a glass jar and the temperature was lowered until clouds of crystals appeared at the bottom of the jar. 20 ml sample each of biodiesel and oil was

poured into a beaker, corked and kept in a refrigerator to solidify. When the sample was brought out and kept in the open, the temperature at which it melts and starts flowing was noted.

2.4. Instrumental characterization

Fourier transfer infrared analysis was carried out using FTIR 8400S spectrophotometer for the determination of functional groups present in biodiesel.

2.5. Design of Experiment

Design Expert software (version 8.0.7.1) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was a central composite design (CCD) a two-level-four-factor ($2^4 + 2 * 4 + 6$), including 30 experiments. Methanol/oil molar ratio, A, Catalyst concentration, B, reaction temperature, C, and reaction time, D were selected as independent factors for the optimization study. The response chosen was the methyl ester yields obtained from transesterification of refined cottonseed oil. The coded values of the process variables were determined by the following equation:

$$X_i = \frac{x_o - x_i}{\Delta x} \quad (10)$$

where x_i – coded value of I^{th} variable, X_i – un-coded value of the I^{th} test variable, Δx – difference between the proceeding values and x_o – un-coded value of the I^{th} test variable at the center point. The factor levels with the corresponding real values and the design matrix are shown in Table 1. The matrix for the four variables was varied at five levels ($-\alpha$, -1 , 0 , $+1$, and $+\alpha$). As usual, the experiments were performed in random order to avoid systematic error. The regression analysis was performed to estimate the response function as a second-order polynomial: [2].

$$Y = \beta_o + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1, i < j}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j \quad (11)$$

where Y is the predicted response, and β_i , β_{ii} , and β_{ij} are coefficients estimated from regression. They represent the linear, quadratic and interactions of the independent variables on the response.

Selection of levels for each factor was based on the experiments performed to study the effects of process variables on the application of homogeneous catalysts for transesterification reaction of refined cottonseed oil (see Table 2).

Table 1 Independent variables and levels used for response surface design.

Independent variables	Symbols	Range and levels				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Methanol oil ratio (v/v)	A	3:1	4:1	5:1	6:1	7:1
Catalyst weight (%)	B	0.2	0.4	0.6	0.8	1.0
Temperature (°C)	C	20	30	40	50	60
Reaction time (min)	D	25	35	45	55	65

3. Results and discussions

3.1. Characterization of results

3.1.1. Physicochemical characteristics

The results of the physicochemical characteristics of the cottonseed oil and biodiesel, along with the standard ASTM D6751-02 [7], are presented in Table 3. The major characteristics (kinematic viscosity, acid value, free fatty acid) are in good agreement with the standard.

From Table 3, it was observed that the specific gravity of refined cottonseed oil was reduced from 0.9076 to 0.8817 after transesterification and it is within the acceptable limit. Saponification value of cottonseed oil is 187.94 mg/g while that of biodiesel is 165.43 mg/g, implies that the triglycerides of cottonseed oil have higher molecular weight of fatty acids (saturated and unsaturated). This result obtained compares favourably with the saponification value of palm oil (187–205), olive oil (185–187), and soy oil (187–193) [8]. Saponification is most important in checking adulteration. The iodine value for cottonseed oil was 68.91 mgI₂; this justifies the fact that the oil is edible. Iodine value for edible oil is less than 100 mgI₂. In general, the greater the iodine value, the higher the degree of unsaturation and the higher the tendency of the oil to undergo oxidative rancidity. Even though the biodiesel has the iodine value of 125.28 mgI₂/g, which is relatively high according to Europe's EN 14214 specifications of iodine value, it indicates that cottonseed oil is a good source of raw material for biodiesel production because the higher the iodine value the more the number of unsaturated double bond present in molecular structure and less the viscosity of the oil [8].

Peroxide value is less suitable in monitoring oxidation and is not specified in the biodiesel standards [8] but it influences cetane number, a parameter that is specified in the fuel standard. An increase in peroxide value involves an increase in cetane number and therefore may reduce ignition delay time [8].

3.1.2. FTIR spectra

The FTIR spectra of biodiesel from cotton seed oil was carried out. From the result, discernable peaks of note were recorded at 3760.0–3472.29 cm⁻¹ (O–H strong stretch), 2927.48–2859.37 cm⁻¹ (C–H weak stretch), 2354.37 cm⁻¹ (C–H weak finger print region/phenyl ring substitution), 1742.41 cm⁻¹ (C–O medium stretch/esters), 1362.62 cm⁻¹ (O–H weak double bending/alkynes), 1176.10–1016.83 cm⁻¹ (C–C/C–O weak stretch/alcohol), 871.50 cm⁻¹ (C–C strong bend/aromatics), 720.10 cm⁻¹ (C–H weak rocking/alkanes) and 592.22–366.06 cm⁻¹ (O–H broad bend/alcohol).

3.2. Evaluation of regression model for transesterification efficiency

The correlation between the experimental process variables and the transesterification efficiency was evaluated using the CCD modelling technique. Second order polynomial regression equation was fitted between the response (Transesterification efficiency, Y) and the process variables: methanol – oil molar ratio, A, catalyst weighty, B reaction temperature, C

Table 2 Experimental set up for 2-level-4-factor response surface design and the experimental and predicted values for biodiesel production from cottonseed oil.

Run order	Alcohol-oil ratio (mol) A		Catalyst (wt%) B		Temperature (°C) C		Time (min) D		Yield (%)	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Exptal	Pred
1	-1	4:1	-1	0.4	-1	30	-1	30	71.40	71.58
2	+1	6:1	-1	0.4	-1	30	-1	30	76.87	76.96
3	-1	4:1	+1	0.8	-1	30	-1	30	73.04	72.46
4	+1	6:1	+1	0.8	-1	30	-1	30	85.69	88.08
5	-1	4:1	-1	0.4	+1	60	-1	30	86.59	86.79
6	+1	6:1	-1	0.4	+1	60	-1	30	87.87	84.42
7	-1	4:1	+1	0.8	+1	60	-1	30	88.32	87.92
8	+1	6:1	+1	0.8	+1	60	-1	30	96.00	95.79
9	-1	4:1	-1	0.4	-1	30	+1	60	74.70	74.63
10	+1	6:1	-1	0.4	-1	30	+1	60	80.12	80.25
11	-1	4:1	+1	0.8	-1	30	+1	60	75.76	77.75
12	+1	6:1	+1	0.8	-1	30	+1	60	94.01	93.63
13	-1	4:1	-1	0.4	+1	60	+1	60	86.65	83.08
14	+1	6:1	-1	0.4	+1	60	+1	60	80.41	80.96
15	-1	4:1	+1	0.8	+1	60	+1	60	87.17	86.46
16	+1	6:1	+1	0.8	+1	60	+1	60	95.23	94.58
17	- α	12:1	0	0.6	0	45	0	45	70.09	69.96
18	+ α	12:1	0	0.6	0	45	0	45	84.54	83.46
19	0	5:1	- α	0.2	0	45	0	45	65.20	65.96
20	0	5:1	+ α	1.0	0	45	0	45	82.12	80.46
21	0	5:1	0	0.6	- α	25	0	45	84.32	80.63
22	0	5:1	0	0.6	+ α	80	0	45	94.42	96.79
23	0	5:1	0	0.6	0	45	- α	120	95.61	94.29
24	0	5:1	0	0.6	0	45	+ α	120	95.04	96.13
25	0	5:1	0	0.6	0	45	0	45	92.10	94.33
26	0	5:1	0	0.6	0	45	0	45	93.04	94.33
27	0	5:1	0	0.6	0	45	0	45	94.15	94.33
28	0	5:1	0	0.6	0	45	0	45	95.60	94.33
29	0	5:1	0	0.6	0	45	0	45	95.80	94.33
30	0	5:1	0	0.6	0	45	0	45	95.70	94.33

Table 3 Characterization of refined cotton seed oil, biodiesel from cotton seed oil and ASTM standard.

S/N	Properties	Units	Refined cottonseed oil	Biodiesel from cottonseed oil	ASTM D6751 standard
1	Moisture content	% wt	0.020	0.020	0.050 max
2	Acid value	Mg/KOHg	0.24	0.22	-
3	FFA	%	0.12	0.11	-
4	Saponification value	Mg/g	187.94	165.43	-
5	Ester value	Mg/g	187.72	165.19	-
6	Iodine value	mgI ₂ /100 g	68.91	125.28	-
7	Peroxide value	Meq/kg	80.00	26.01	-
8	Specific gravity		0.9076	0.8817	0.88
9	Kinematic viscosity	mm ² /s	29.22	6.81	1.9–6.0
10	Odour		Agreeable	Agreeable	-
11	Colour		Brown	Light brown	-
12	Refractive index	(28 °C)	1.4233	1.344	-
13	Flash point	(°C)	255	173	100–170
14	Cloud point	(°C)	-3.0	7.0	-3–12
15	Pour point	(°C)	-2.3	5.0	-15–10
16	Fire point	(°C)	-	193	-
17	Cetane number			56.06	48–65
18	High heating value	MJ/kJ	41.25	39.54	-

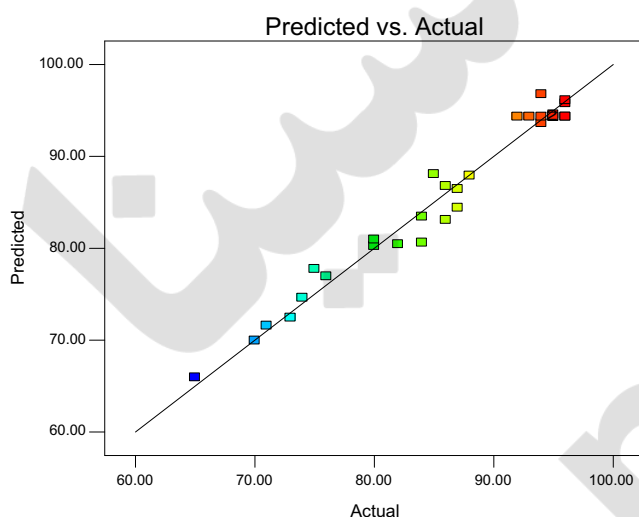
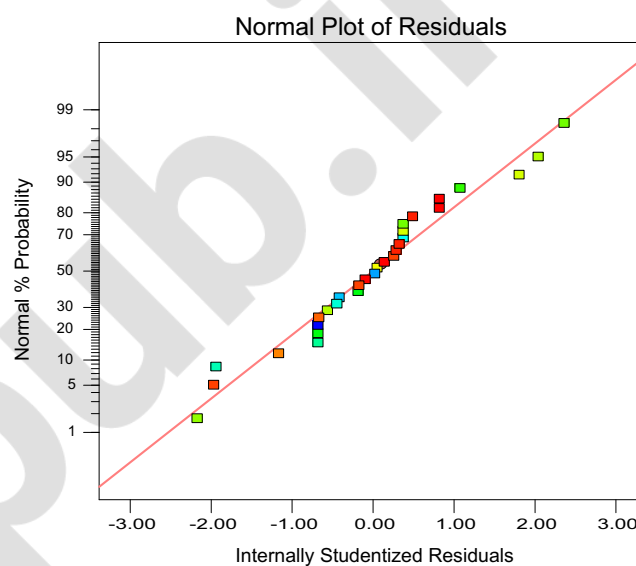
and reaction time, D. From Table 4, the ANOVA results showed that the quadratic model is suitable to analyse the experimental data. The model in terms of the coded values of the process parameters is given by:

$$Y = 94.33 + 3.37A + 3.62B + 4.04C + 0.46D + 2.56AB - 1.94AC + 0.63AD + 0.63BC + 0.56BD - 1.69CD - 4.41A^2 - 5.28B^2 - 1.41C^2 + 0.22D^2 \quad (12)$$

Table 4 Analysis of variance (ANOVA) for the fitted quadratic polynomial model.

Source of variables	Sum of squares	DF	Mean squares	F-value	P-value Prob > F
Model	2401.88	14	171.56	35.21	< 0.0001 significant
A	273.37	1	273.37	56.11	< 0.0001
B	315.37	1	315.37	64.73	< 0.0001
C	392.04	1	392.04	80.46	0.0001
D	5.04	1	5.04	1.03	0.3252
AB	105.06	1	105.06	21.56	0.0003
AC	60.06	1	60.06	12.33	0.0032
AD	0.063	1	0.063	0.013	0.9113
BC	0.063	1	0.063	0.013	0.9113
BD	5.06	1	5.06	1.04	0.3242
CD	45.56	1	45.56	9.35	0.0080
A ²	532.53	1	532.53	109.3	< 0.0001
B ²	765.03	1	765.03	157.02	< 0.0001
C ²	54.24	1	54.24	0.11.13	0.0045
D ²	1.31	1	1.31	0.27	0.6113
Residual	73.08	15	4.87		
Lack of fit	59.75	10	59.75	2.24	0.1905 not significant
Pure error	13.33	5	2.67		
Cor total	2474.97	29			

Std dev. 2.21, $R^2 = 0.9705$, mean 85.63, Adj $R^2 = 0.9629$, C.V.% 2.58, Pred $R^2 = 0.9532$.
PRESS 363.36, Adeq precision = 19.755.

**Figure 1** Predicted versus actual FAME yield.**Figure 2** Normal probability plot of the residual.

To develop a statistically significant regression model, the significance of the regression coefficients was evaluated based on the p -values. The coefficient terms with p -values more than 0.05 were insignificant and were removed from the regression model. The analysis in Table 4 shows that the linear terms A, B, and C; the quadratic terms, A², B², and C² and the interaction terms of AB, AC and CD; are significant model terms but D was included in the model because of its importance. The model was reduced to Eq. (13) after eliminating the insignificant coefficients.

$$Y = 94.33 + 3.37A + 3.62B + 4.04C + 0.46D + 2.56AB - 1.94AC + 0.56CD - 4.41A^2 - 5.28B^2 - 1.41C^2 \quad (13)$$

The analysis of variance indicated that the quadratic polynomial model was significant and adequate to represent the actual relationship between transesterification efficiency and the significant model variables as depicted by very small p -value (< 0.0001). The significance and adequacy of the established model were further elaborated by a high value of coefficient of determination (R^2) value of 0.9705 and adj. R^2 value of 0.9629. This means that the model explains 97.05% of the variation in the experimental data. The adequate correlation between the experimental values of the independent variable and predicted values further showed the adequacy of the model.

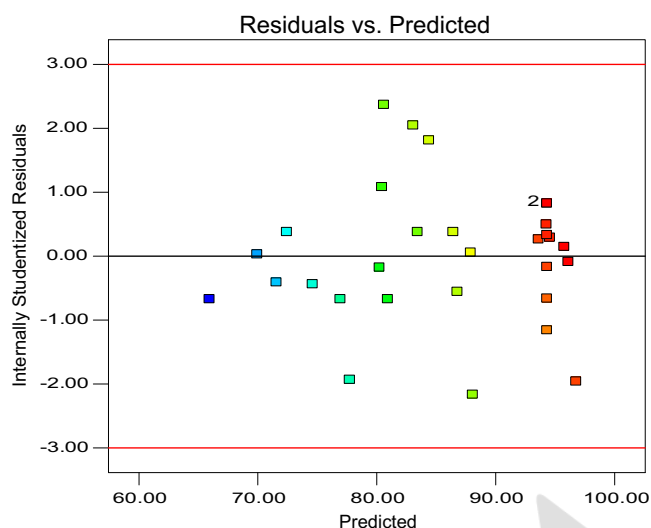


Figure 3 Plot of residual versus predicted response.

3.3. Response surface estimation

The interactive effects of the process variables on the transesterification efficiency were studied by plotting three dimensional surface curves against any two independent variables, while keeping other variables at their central (0) level. The

3D curves of the response (transesterification efficiency) from the interactions between the variables are shown in Figs. 4–6. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response. The elliptical shape of the curves indicates a good interaction of the two variables and circular shape indicates no interaction between the variables. The curves obtained in this study showed that there is a relative significant interaction between all the variables. Optimum conditions were also obtained from the response surface plots. The stationary point or central point is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour levels in each of the plots will correspond to the optimum values of the respective variables. The maximum predicted yield is indicated by the surface confined in the smallest curve of the contour diagram. The optimum values of the variables were: reaction temperature, 55 °C; reaction time, 60 min; catalyst weight 0.6% and methanol oil molar ratio 6:1. The predicted response value at these optimum values was 95.57%. To confirm this optimum values, experiments were performed at these values and the experimental response value was 96.99%. This showed that the model correctly explains the influence of the process variables on the production of FAME from cotton seed oil.

The lack of fit test with p -value of 0.1905, which is not significant (p -value > 0.05 is not significant) showed that the model satisfactorily fitted to the experimental data. Insignifi-

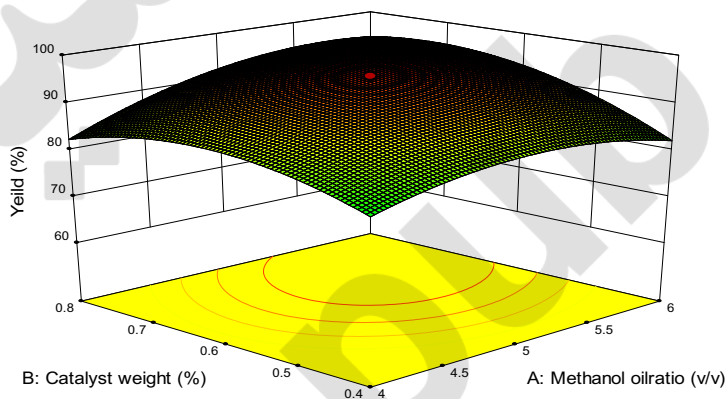


Figure 4 Surface plot between catalyst weight and molar ratio against biodiesel yield.

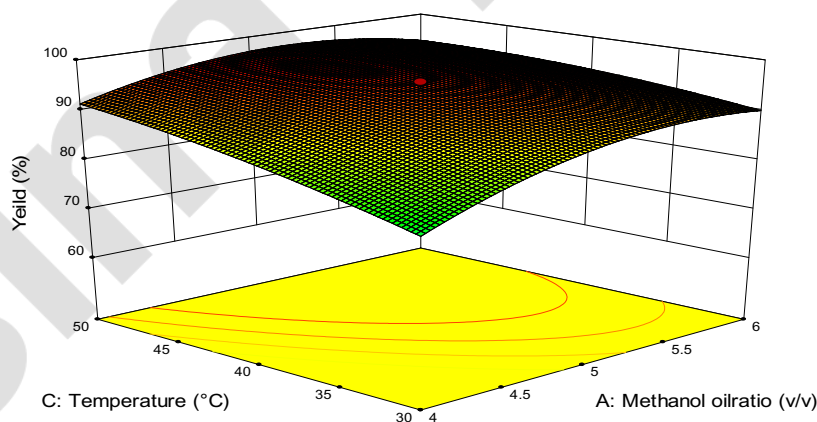


Figure 5 Surface plot between molar ratio and temperature against biodiesel yield.

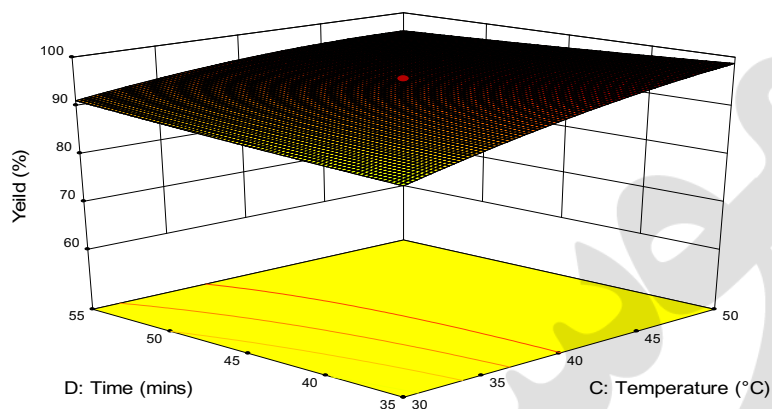


Figure 6 Surface plot between time and temperature against biodiesel yield.

cant lack of fit is mostly needed because significant lack of fit indicates that there might be contributions in the regression-response relationship that is not accounted for by the model. The predicted values versus actual values for the biodiesel yield with adjusted- R^2 value of 0.9629 shows the model with 96.29% of variability (Fig. 1). The predicted value and the experimental values were in reasonable agreement (R^2 close to unity), which means that the data fit well with the model and give a convincingly good estimate of response for the system in the range studied. In addition, investigation on residuals to validate the adequacy of the model was performed. Residual is the difference between the observed response and predicted response. This analysis was examined using the normal probability plot of residuals (Fig. 2) and the plot of the residual versus predicted response (Fig. 3). The normal probability plot of the residuals shows that the errors are distributed normally in a straight line and insignificant. On the other hand, the plot of residuals versus predicted response showed a structure less plot suggesting that the model is adequate and that the model does not show any violation of the independence or constant variance assumption hence conforming to the literature by Lee, et al. [9].

4. Conclusions

In this work a study of the optimization of cotton seed oil transesterification reaction parameters was carried out by response surface methodology (RSM). The process parameters for transesterification reaction such as: methanol oil molar ratio, KOH catalyst effect, temperature and reaction time were investigated. The analysis of variance (ANOVA) showed that a satisfactory result was obtained. Moreover, increasing both temperature and KOH concentration higher conversion rate

was achieved and time does not seem to have any significant effect. The statistical models developed for predicting yield showed a good agreement between the experimental and calculated values (≥ 0.96), demonstrating the usefulness of regression analysis as a tool for optimization purposes. The experimental results suggested the optimal condition as follows: methanol/oil molar ratio, 6:1; temperature, 55 °C; time, 60 min; catalyst concentration, 0.6%. This optimized condition was validated with the actual biodiesel yield in 96%.

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