

Response Surface Methodological Optimization of Biodiesel Production from *Cassia tora* Seed

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Abstract: Two stage biodiesel production process (esterification and transesterification) was performed on *Cassia tora* seed oil extract in accordance with Association of Official Analytical Chemist method. Eighty grams (80 g) of the seed sample and 500 ml of petroleum ether solvent yields 8.24% *Cassia tora* oil (CTO). Response Surface Methodology (RSM) optimization was accomplished by 5-level 4-factorial Central Composite Design (CCD) in 30 runs, using 7.0 version of the design expert software and interaction effects of methanol/oil ratio (A), catalyst concentration (B), temperature (C) and reaction time (D) were studied on the esterification and transesterification processes. The high free fatty acid (FFA) of 2.6 mgKOH/g of CTO was reduced through CCD design of experiment to 0.395 mgKOH/g and validated to be 0.40 mgKOH/g using the optimum process variable of methanol/oil ratio (6:1), H₂SO₄ catalyst (1.60 v/v) in 93 minutes at 45 °C. Experimentally validated *Cassia tora* biodiesel (CTB) yield of 92.4% was obtained from CCD predicted value of 95.9%, using methanol/oil molar ratio (9:1), NaOH catalyst (0.8 w/w) in 120 minutes at 50 °C. The analysis of variance (ANOVA) of CTO free fatty acid minimization (esterification) and CTB maximization (transesterification) both gives second-order model equations respectively as the best fits of experimental data.

Keywords: Analysis of variance, biodiesel, *Cassia tora* seed, Central Composite Design and Response Surface Methodology.

1.0 INTRODUCTION

The continued and increasing use of diesel derived from fossil oil intensifies air pollution and magnifies the global warming problem caused by CO₂ and other particulate matters [1,2]. This level of fossil fuel emissions is unacceptable and unsustainable. Therefore, liquid biofuel particularly biodiesel is being increasingly considered an alternative to diesel fuel as an energy source, owing to its potential to reduce environmental stress caused by fossil fuel use [3,4]. Biodiesel potential of *Cassia tora* was reported by [5], where it was classified among the twenty-seven (27) potentials non-edible biodiesel feedstock.

Biodiesel as the most promising alternative diesel fuel has received considerable attention because of its biodegradability, renewability, non-toxicity and low emissions

of gaseous and particulate pollutants with a higher cetane number than petro-diesel [6]. In addition, it meets the currently increasing demands of world energy and provides energy security that in a large degree is dependent on petroleum-based fuel resources, which will be depleted in the next foreseeable future if the present pattern of energy consumption continues [7].

Biodiesel has higher oxygen than petroleum diesel and its use in diesel engines has shown great reductions in emissions of particulate matters, carbon monoxide, smoke and noise. In addition, burning of vegetable oil-based fuel does not contribute to net atmospheric carbon dioxide levels because such fuels are made from agricultural material which are produced via photosynthetic carbon fixation [8].

In the optimization studies of biodiesel production process from *Cassia tora* seed oil the effects of variables including methanol/oil molar ratio, catalysts concentration, reaction temperature and reaction time in minimizing *Cassia tora* oil Free Fatty Acid (FFA) content and maximizing *Cassia tora* biodiesel yield will be examined using the Response Surface Methodology (RSM) which is multivariable technique in use in analytical optimization [9]. The eventual objectives of the RSM are to determine the optimum operating conditions for the system or to determine the region, which satisfied the operating specifications [10].

The aim of this research is production of biodiesel from *Cassia tora* seed oil via 2-step acid-base catalyzed method and the process optimization with specific objectives include Minimization of FFA in extracted oil and maximization of biodiesel yield using RSM design of experiment.

2.0 LITERATURE REVIEW

2.1 *Cassia tora*

The cassia plant is a large genus and is classified as a legume under the family leguminosaceae or as a weed in the family caesalpincaceae. Cassia species include *cassia alata*, *cassia august*, *cassia folia*, *cassia fistula*, *cassia occidentalis*, *cassia senna* and *cassia tora*. The plant is found enormously in

most tropical countries; it is a draught resistant plant and can grow on low fertile wasteland [11]. *Cassia tora* is mostly found in South-East Asia and South West Pacific as an important weed. *Cassia tora* is considered a wild weed that has many healing benefits. The plant can grow 30-90 cm (12-35 in.) tall and consists of alternative pinnate leaves that grow up to 3-

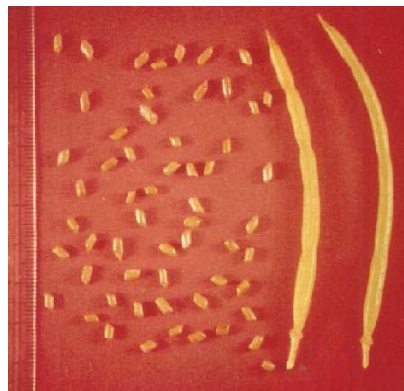
4.5 cm long. The stem has distinct smelling foliage when young while the flowers are in pairs in axils of leaves with five petals and yellow in colour [12]. The seeds are also used as a mordant in dyeing [13]. Plates 1(a), 1(b) and 1(c) show *Cassia tora* plant, *Cassia tora* seed and *Cassia tora* pods and seeds respectively.



(a): *Cassia tora* Plant



(b): *Cassia tora* Seeds



(c): *Cassia tora* Pods and Seeds

Plate 1: *Cassia tora* Plant, Seeds and Pods [12]

2.2 Potential Technology for Biodiesel Production

There are different processes which can be applied to synthesize biodiesel, such as direct use and blending [8], micro emulsion process [14], thermal cracking process or pyrolysis [15], Esterification and the most conventional transesterification process. This is because the method is relatively easy, can be carried out at moderate condition, and gives the best conversion efficiency and quality of the produced fuel [16].

Esterification Mechanism

Esterification occurs when a carboxylic acid reacts with an alcohol to produce ester. This reaction can only occur in the presence of an acid catalyst and heat. It takes a lot of energy to remove hydrogen from carboxylic acid to create space for a methyl group to form an ester, so a catalyst and heat are needed to produce the necessary energy. The most widely used catalysts are Concentrated tetraoxosulphate (VI) and hydrochloric acids. Esterification as a chemical process is widely employed in biodiesel industries to reduce the percentage free fatty acid of an oil feed stock prior to base

catalytic stage in biodiesel production [17]. The complete esterification process is shown in Eq. 1:



where R and R' are the alkyl group.

Transesterification Mechanism

In transesterification, the carboxylic carbon of starting ester (RCOOR') undergoes nucleophilic attack by the incoming alkoxide (R²O⁻) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the transesterified product (RCOOR²). The various species exist in equilibrium, and the product distribution depends on the relative energies of the reactants and products [8]. Biodiesel production process with all species in their chemical structures where process reaction mechanism can be easily drawn as shown in Fig. 1:

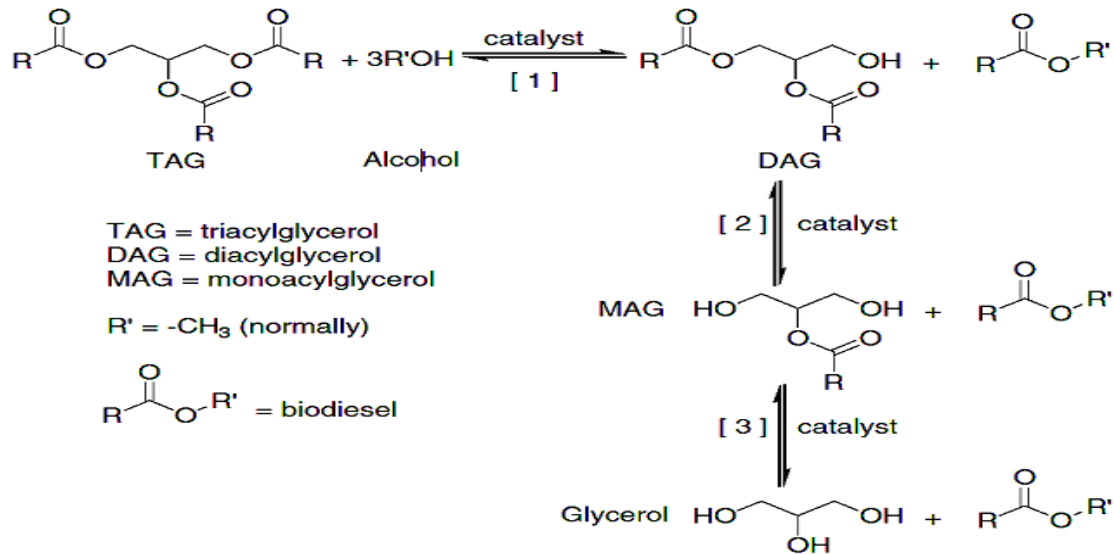


Figure 1: Biodiesel production process [8]

2.3 Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques in which a response of interest is influenced by several variables and the objective is to optimize this response using any of the model of Eqs. 2 or 3 [18].

$$y = f(x_1, x_2) + \epsilon \quad (2)$$

where ϵ represents the noise or error observed in the response y and surface represented by $\eta = f(x_1, x_2)$, which is called a response surface and

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

where y is the predicted response, β_0 is the intercept, β_i is the linear coefficients, β_{ij} is the interaction coefficients, β_{ii} is the quadratic coefficients while x_i , x_j and x_i^2 are the coded values of the experimental variables.

The main objective of RSM is to optimize the response [19] which are usually represented graphically called surface response, where η is plotted versus the levels of x_1 and x_2 , to help visualize the shape of a response. In the contour plot, lines of constant response are drawn in the x_1 & x_2 planes, each contour corresponds to a particular height of the response surface.

3.0 EXPERIMENTAL PROCEDURE

3.1 *Cassia tora* seeds and reagents/chemicals

The seeds were collected at different locations within Bauchi Town Metropolis, Northeast-Nigeria and

authenticated. All reagents/chemicals used were of analytical grade from Sigma Aldrich, England purchased from vendors in Bauchi State.

3.2 Experimental design and optimization by response surface methodology

The experimental design and optimization were carried out according to the two stages involved in the synthesis as follows:

A 5-level 4-factors experiment was conducted using a central composite design (CCD) to examine the effects of methanol/oil molar ratio (v/v), catalyst concentration (%), temperature of the reaction (°C) and time of reaction (min) to minimized free fatty acid (FFA) level in stage-1 and maximized *Cassia tora* biodiesel (CTB) yield in stage-2 of the experiment. Stirring rate was kept constant at 500 r/min throughout the experiment, due to the fact that it has less effect on the overall biodiesel yield [20]. The CCD consisted of 30 experimental runs in each stage with 24 non-centre points and six replicated centre points, which provided sufficient information to fit a full second order polynomials model. The design expert 7.0 software was employed to analyze the data for developing response equations, for analysis of variance (ANOVA), general surface plots and determined optimum conditions using its optimization toolbox.

For each factor in each stage, 5-levels were defined, and their values designated by the codes: -2, -1, 0, +1 and +2 as shown in Tables 1 and 2 for esterification and transesterification respectively.

Table 1: Constraints Used in CCD with the Objective of Minimizing Free Fatty Acid (Esterification)

Variable	Name	Unit	Coded levels				
			-2	-1	0	+1	+2
A	Methanol/oil	v/v	3	5	7	9	11
B	Catalyst(H ₂ SO ₄)	v/v %	1.2	1.4	1.6	1.8	2.0
C	Temperature	°C	40	45	50	55	60
D	Reaction time	(min)	30	60	90	120	150

Table 2: Constraints Used in CCD with the Objective of Maximizing *Cassia tora* Biodiesel Yield (Transesterification)

Variable	Name	Unit	Coded levels				
			-2	-1	0	+1	+2
A	Methanol/oil	v/v	3	5	7	9	11
B	Catalyst (NaOH)	w/w %	0.4	0.6	0.8	1.0	1.2
C	Temperature	°C	40	45	50	55	60
D	Reaction time	(min)	30	60	90	120	150

3.3 Acid catalyzed stage-1 procedure (esterification)

Esterification reaction was carried out in a 250 ml round bottom flask as the reactor. The reactor was fitted with a reflux condenser (to minimize alcohol loss), a magnetic stirrer which double as temperature regulator served as the heating mantle. Oil was pre-heated to 110 °C for 30 minutes to drive off water (that might have been present in it during extraction) before being charged into the reactor. Calculated amounts of methanol and concentrated tetraoxosulphate (VI) acid was mixed separately and transferred into the reactor, a stirring bit was inserted for proper mixing. Experimental conditions were set according to the combination given by the design layout generated using the design expert 7.0 software. At the end of the reaction the mixture was allowed to stand for 2 hours in a separating funnel while the lower layer was collected as oil for transesterification process.

3.4 Base catalyzed stage-2 procedure (transesterification)

Transesterification reaction was carried out in a 250 ml round bottom flask as a reactor. The reactor was fitted with a reflux condenser (to minimize alcohol loss), a magnetic stirrer which double as temperature regulator served as the heating mantle. Esterified oil was pre-heated at 110 °C for 30 minutes to drive off water before being charged into the reactor. Calculated amounts of methanol and sodium hydroxide were dissolved separately, and the mix was transferred into the reactor, a stirring bit was inserted for proper mixing. Experimental conditions were set according to the combination given by the design layout generated using the design expert 7.0 software. At the end of the reaction the mixture was allowed to stand for 2 hours in a separating funnel. The upper layer which is *Cassia tora* biodiesel was decanted into a separate beaker while the lower layer which comprises of glycerol and soap was collected from the bottom of the funnel. The percentage yield of biodiesel produced was calculated using Eq. 4 [1]:

$$\%Biodiesel\ yield = \frac{volume\ of\ biodiesel\ produced}{volume\ of\ oil\ sample\ in\ the\ process} \tag{4}$$

4.0 RESULTS AND DISCUSSION

4.1 Acid Catalyzed FFA Reduction (Esterification)

The CCD standardization of process variables involved in FFA reduction process was carried out in accordance with the design layout. Thirty (30) experimental runs were conducted and predicted responses obtained as presented in Table 3. The predicted responses of FFA reduction were calculated using

the regression model (Eq. 5) generated. From Table 3 it was observed that low residual errors were recorded between the experimental and predicted responses which ranges between 0.00-0.13 %, which indicates agreement between experimental and predicted responses and thus proved the reliability of the model for predicting responses.

Table 3: Central Composite Design Responses for FFA Reduction (Esterification)

Run	A: Methanol/oil (v/v)	B: Catalyst (H ₂ OS ₄) (v/v)	C: Temperature (°C)	D: Time (min)	FFA Reduction Response (mgKOH/g)		
					Experimental	Predicted	Residual
1	7.00	1.60	50.00	30.00	1.51	1.49	0.02
2	5.00	1.80	55.00	120.00	1.22	1.18	0.04
3	9.00	1.80	55.00	60.00	0.98	0.99	0.01
4	9.00	1.40	45.00	120.00	0.84	0.91	0.07

5	7.00	1.60	50.00	90.00	0.48	0.49	0.01
6	11.00	1.60	50.00	90.00	0.60	0.57	0.03
7	5.00	1.40	45.00	60.00	0.40	0.53	0.13
8	9.00	1.80	55.00	120.00	1.04	0.97	0.07
9	9.00	1.40	55.00	120.00	1.20	1.19	0.01
10	5.00	1.80	55.00	60.00	1.18	1.16	0.02
11	9.00	0.80	45.00	120.00	0.82	0.84	0.02
12	7.00	1.60	50.00	90.00	0.50	0.49	0.01
13	5.00	1.80	45.00	120.00	0.82	0.88	0.06
14	9.00	1.40	55.00	60.00	1.08	1.07	0.01
15	7.00	1.60	40.00	90.00	0.55	0.43	0.12
16	7.00	1.60	50.00	90.00	0.50	0.49	0.01
17	5.00	1.40	55.00	60.00	1.04	0.97	0.07
18	7.00	2.00	50.00	90.00	1.00	1.01	0.01
19	9.00	1.80	45.00	60.00	0.80	0.86	0.06
20	3.00	1.60	50.00	90.00	0.48	0.50	0.02
21	7.00	1.20	50.00	90.00	0.90	0.88	0.02
22	9.00	1.40	45.00	60.00	0.80	0.80	0.00
23	7.00	1.60	50.00	150.00	1.60	1.62	0.02
24	5.00	1.40	55.00	120.00	1.12	1.12	0.00
25	5.00	1.80	45.00	60.00	0.90	0.87	0.03
26	7.00	1.60	50.00	90.00	0.48	0.49	0.01
27	7.00	1.60	60.00	90.00	0.90	1.01	0.11
28	5.00	1.40	45.00	120.00	0.74	0.68	0.06
29	7.00	1.60	50.00	90.00	0.50	0.49	0.01
30	7.00	1.60	50.00	90.00	0.50	0.49	0.01

Fitness of regression equation and analysis of variance(ANOVA) for FFA reduction

Based on the CCD design and results of experiments in Table 3, regression analysis generated the following

$$FFA = +0.49 + 0.016A + 0.031B + 0.14C + 0.032D - 0.014AB - 0.014AC - 8.750E - 003AD - 0.036BC - 0.034BD - 1.250E - 003CD + 0.010A^2 + 0.11B^2 + 0.057C^2 + 0.27D^2 \dots (5)$$

where FFA is the response (%), and the coded terms A, B, C & D represent methanol/oil ratio, catalyst (v%), temperature (°C) & reaction time (min) respectively. From the model equation, the linear terms A, B, C, D and the quadratic terms A², B², C², D² are positive and which denote significant contribution in FFA reduction while the interaction terms AB, AC, AD, BC, BD, CD are negative which denote negative contribution in FFA reduction, which is in agreement with Prerna *et al.*, [21].

Table 4a give the lack of fit test with Quadratic model been suggested having probability value (p-value) of <0.0001. The estimated coefficients of regression model are given in Table 4b. The large value of the coefficient of multiple determinations (R²=0.9741) indicate good fitness of the result.

quadratic regression model equation based on coded factors as shown in Eq. 5.

The high adjusted and predicted R² values of 0.9499 and 0.8517 respectively revealed that the model adequately represents the experimental result. The effect of the variables as linear, quadratic or interaction coefficients on the response were tested for significance by ANOVA as shown in Table 4c. It was observed that the variable with most significance effect on the FFA reduction were the linear terms of temperature (p<0.0001) and catalyst concentration (p<0.0001), followed by the quadratic terms of catalyst concentration (p<0.0001) and reaction time (p<0.0001). The least significant term that has minimal contribution in FFA reduction is the interaction term CD (p<0.9446) while in general the model having an F-value of 40.31 and p<0.0001 is significant.

Table 4: Regression Analysis for FFA Reduction

(a): Lack of Fit Tests for FFA Reduction

Source	Sum of Squares	Df	Mean Square	F-Value	P-value; Prob>F
Linear	2.35	20	0.12	1102.27	<0.0001
2FI	2.21	14	0.16	1478.68	<0.0001

Quadratic	0.075	10	7.452E-003	69.87	<0.0001	Suggested
Cubic	0.011	2	5.662E-003	53.09	0.0004	Aliased
Pure Error	5.333E-004	5	1.067E-004			

(b): Model Summary Statistics for FFA Reduction

Source	Std. Dev.	R-Square	Adjusted R-Square	Predicted R-Square	PRESS	
Linear	0.31	0.1888	0.0590	-0.1381	3.30	
2FI	0.34	0.2382	-0.1628	-0.2885	3.74	
Quadratic	0.071	0.9741	0.9499	0.8517	0.43	Suggested
Cubic	0.041	0.9959	0.9831	0.4373	1.63	Aliased

(c): Analysis of Variance (ANOVA) for FFA Reduction

Source	Sum of Squares	Df	Mean Square	F-Values	P-value; Prob>F
Model	2.82	14	0.20	40.31	<0.0001
A-Methanol	6.017E-003	1	6.017E-003	1.20	0.2901
B-Catalyst	0.023	1	0.023	4.56	0.0496
C-Temperature	0.49	1	0.49	98.54	<0.0001
D-Reaction Time	0.025	1	0.025	5.07	0.0398
AB	0.076	1	0.076	15.11	0.0015
AC	0.027	1	0.027	5.44	0.0340
AD	1.225E-003	1	1.225E-003	0.24	0.6279
BC	0.021	1	0.021	4.20	0.0583
BD	0.018	1	0.018	3.64	0.0757
CD	0.500E-005	1	0.500E-005	4.996E-003	0.9446
A ²	2.976E-003	1	2.976E-003	0.59	0.4526
B ²	0.35	1	0.35	69.89	<0.0001
C ²	0.088	1	0.088	17.60	0.0008
D ²	1.93	1	1.93	386.15	<0.0001
Residual	0.075	15	5.004E-003		
Lack of Fit	0.075	10	7.452E-003	69.87	<0.0001
Pure Error	5.333E-004	5	1.067E-004		

R-Square: 0.9741 and Adjusted R-Square: 0.9499

4.2 Response surface plots for FFA reduction (esterification)

The predicted vs. actual, perturbation and surface plots were used in this section to describe the trend in FFA reduction response when methanol/oil ratio, catalyst concentration, reaction temperature and reaction time are either increased or decreased.

Relationship between predicted and actual response

Figure 2 shows the plot between the predicted and actual FFA values, the linear graph generated by the design expert software indicates agreement between the predicted and actual experimental values.

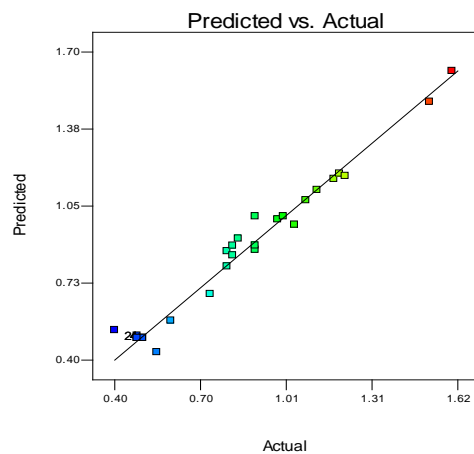


Figure 2: Predicted response versus actual experimental response

Interaction between catalyst and Methanol/oil ratio on FFA

Figure 3 represents a surface contour plot interaction between catalyst and methanol/oil ratio. At a fixed temperature of 50 °C and reaction time of 90 min, the FFA

reduction of 0.46 mgKOH/g was achieved at a catalyst value of 1.60 and a methanol/oil ratio of 5.00.

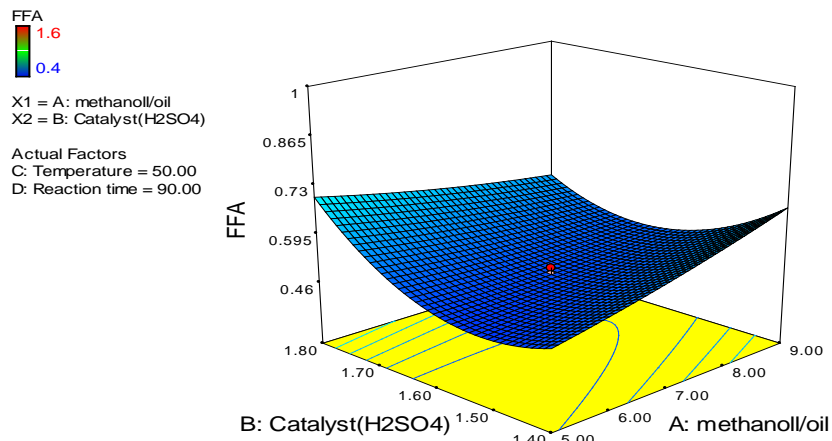


Figure 3: Interaction between catalyst and methanol/oil ratio

Interaction between Temperature and Methanol/oil ratio on FFA

Figure 4 represents a surface contour plot interaction between temperature and methanol/oil ratio. At a fixed catalyst concentration of 1.60 and reaction time of 90 min, the FFA

increased from 0.46 to 0.495 mgKOH/g with increase in both temperature and methanol/oil ratio from 50 °C to 52.50 °C and 5.00 to 7.00 respectively, this can be attributed to high temperatures cause methanol to escape and hindered FFA reduction.

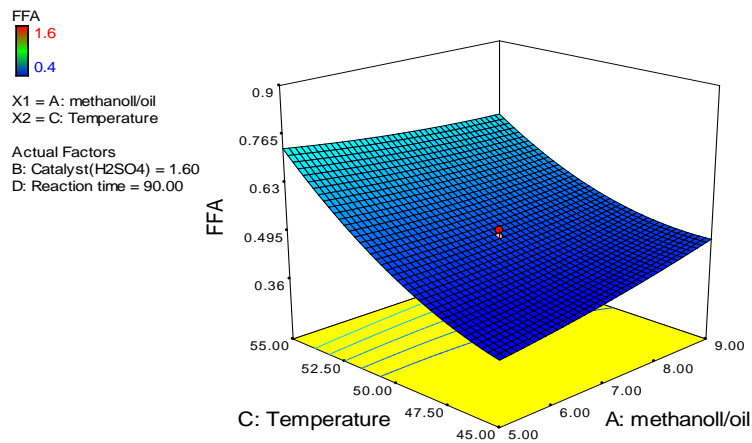


Figure 4: Interaction between temperature and methanol/oil ratio

Interaction between Reaction time and Methanol/oil ratio on FFA

Figure 5 represents a surface contour plot of interaction between reaction time and methanol/oil ratio. At a fixed catalyst of 1.60 v/v and temperature of 50 °C, the FFA

increased to 0.70 mgKOH/g with an increase in reaction time from 90 to 105 min as indicated on the contour. This can be explained base on the fact that, higher reaction time encourages reverse reaction which on the other hand hinders the FFA reduction.

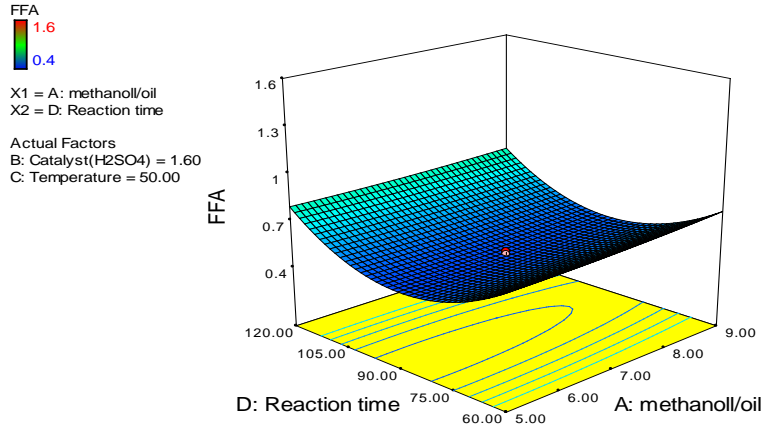


Figure 5: Interaction between reaction time and methanol/oil ratio

Interaction between Temperature and catalyst on FFA

Figure 6 represents a surface contour plot interaction between temperature and catalyst concentration. At a fixed methanol/oil ratio of 7.00 and reaction time of 90 min, the FFA value of 0.39 was recorded at a temperature of 47.50 °C and a

catalyst concentration of 1.60 v/v, this indicate that low temperature and low catalyst concentration favour FFA reduction while higher temperature close to the boiling point of methanol caused methanol escape and hindered FFA reduction.

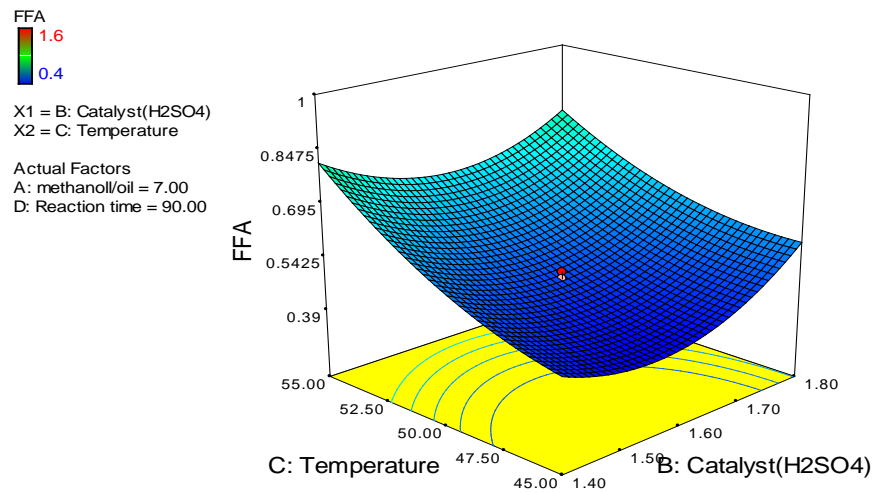


Figure 6: Interaction between temperature and catalyst

Interaction between independents variables (A B C and D in coded terms) on FFA

Figure 7 represents perturbation plot which give the approximate optimum of all the four independent variables as follows; methanol/oil ratio 7:1, catalyst 1.60 v/v , temperature 50 °C and time 90 min. FFA decreases with increase in catalyst, temperature and reaction time till the midpoint is reached, beyond which an increase in catalyst increased the FFA value between 0.7-1.0 mgKOH/g. This could be attributed to addition of excessive acid catalyst which makes

the reaction much slower and hinders FFA reduction. Also, an increase in temperature beyond the midpoint increased FFA value between 0.4-0.7 mgKOH/g. Furthermore, FFA value increases significantly beyond the midpoint with increase in reaction time while methanol/oil ratio has minimal effect on FFA reduction as it does not show any noticeable change on FFA value before and after the midpoint, this could be related to 1:1 carboxylic acid to methanol molar ratio in esterification equation. This result is in agreement to prerna *et al.* [21].

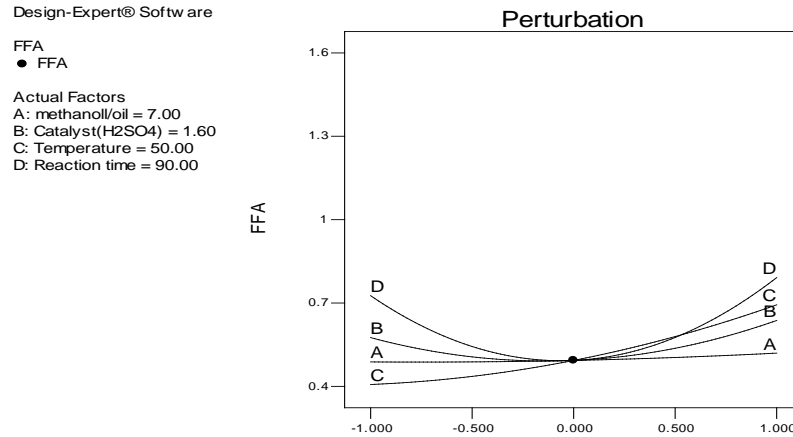


Figure 7: Perturbation plot between response variables on ffa

4.3 Base Catalyzed Biodiesel Production (Transesterification)

The CCD standardization of process variables involved in CTB process was carried out in accordance with the design layout. Thirty (30) experimental runs were conducted and the predicted responses obtained as presented

in Table 5. The predicted responses of CTB were calculated using the regression model (Eq. 6) generated. The Residual error between experimental and predicted response ranges between 0.03-1.37 %, thus the low residual error indicates agreement between experimental and predicted responses.

Table 5: Central Composite Design Responses for CTB Production (Transesterification)

Run	A: Methanol/oil (v/v)	B: Catalyst (NaOH) w/w	C: Temperature (°C)	D: Time (min)	% Cassia tora Biodiesel Responses		
					Experimental	Predicted	Residual
1	9.00	0.60	45.00	60.00	89.60	88.60	1.00
2	5.00	0.60	55.00	60.00	82.10	82.27	0.17
3	7.00	1.20	50.00	90.00	80.43	81.68	1.25
4	5.00	1.00	45.00	120.00	85.12	85.39	0.27
5	7.00	0.80	50.00	30.00	81.20	82.71	1.15
6	5.00	1.00	45.00	60.00	79.50	78.37	1.13
7	5.00	1.00	55.00	120.00	80.10	80.45	0.35
8	5.00	0.60	45.00	60.00	83.40	83.59	0.19
9	9.00	1.00	55.00	60.00	89.60	88.25	1.35
10	9.00	1.00	55.00	120.00	91.60	91.86	0.26
11	7.00	0.80	40.00	90.00	88.40	88.22	0.18
12	9.00	0.60	55.00	120.00	89.20	89.74	0.54
13	9.00	0.60	45.00	120.00	92.50	93.78	1.28
14	7.00	0.80	50.00	150.00	91.20	89.83	1.37
15	3.00	0.80	50.00	90.00	80.55	80.64	0.09
16	7.00	0.80	60.00	90.00	84.00	84.32	0.32
17	7.00	0.80	50.00	90.00	90.30	90.27	0.03
18	5.00	1.00	55.00	60.00	79.35	78.52	0.83
19	7.00	0.80	50.00	90.00	90.14	90.27	0.13
20	5.00	0.60	45.00	120.00	86.33	87.10	0.77
21	7.00	0.40	50.00	90.00	85.99	84.87	1.11
22	7.00	0.80	50.00	90.00	90.50	90.27	0.23
23	9.00	1.00	45.00	60.00	85.20	85.27	0.07
24	9.00	1.00	45.00	120.00	95.20	94.44	0.76
25	7.00	0.80	50.00	90.00	90.14	90.27	0.13
26	7.00	0.80	50.00	90.00	90.40	90.27	0.13
27	11.00	0.80	50.00	90.00	97.00	97.05	0.05
28	9.00	0.60	55.00	60.00	89.45	89.63	0.18

29	5.00	0.60	55.00	120.00	80.80	80.70	0.10
30	7.00	0.80	50.00	90.00	90.20	90.27	0.07

Fitness of regression equation and analysis of Variance (ANOVA) for CTB production

Based on the CCD design and results of experiments in Table 10, regression analysis generated the following quadratic regression model equation based on coded factors (Eq. 6).

$$CTB = +90.27 + 4.10A - 0.77B - 0.97C + 1.78D + 0.59AB + 0.59AC + 0.42AD + 0.37BC + 0.88BD - 1.27CD - 0.36A^2 - 1.76B^2 - 1.00C^2 - 1.00D^2 \dots (6)$$

where, CTB is the Yield (%), and the coded terms A, B, C & D represent methanol/oil ratio, catalyst concentration (w%), temperature (°C) & reaction time (min) respectively. From the model equation that the linear terms A, D and the interaction terms AB, AC, AD and BC are positive which denote significant contribution in CTB while quadratic terms A², B², C², D² and interaction terms BD and CD are negative which denote negative contribution in CTB, which conform to Perna *et al.* [21].

Table 6a give the lack of fit test with Quadratic model been suggested having probability value (p-value) of <0.0001. The estimated coefficients of regression model are given in Table 6b. The large value of the coefficient of multiple determinations (R²=0.9776) indicate good fitness of the result. The high adjusted and predicted R² values of 0.9567 and 0.8717 respectively revealed that the model adequately represents the experimental result. The effect of the variables as linear, quadratic or interaction coefficients on the response were tested for significance by ANOVA as presented in Table 6c. It was observed that the variable with most significance effect on the CTB production were the linear terms of methanol/oil ratio (p<0.0001), catalyst concentration (p<0.0001) and reaction time (p<0.0001), followed by the quadratic term of catalyst concentration (p<0.0001). The least significant term that has minimal contribution in CTB production is the interaction term BC (p<0.1734) while in general the model having an F-value of 46.7 and p<0.0001 is significant.

Table 6: Regression Analysis for CTB Production

(a): Lack of Fit Tests for CTB Production

Source	Sum of Squares	Df	Mean Square	F-Value	P-value; Prob>F	
Linear	182.62	20	9.13	359.68	<0.0001	
2FI	128.44	14	9.17	361.39	<0.0001	
Quadratic	15.56	10	1.56	61.29	<0.0001	Suggested
Cubic	1.13	2	0.57	22.32	0.0032	Aliased
Pure Error	0.13	5	0.025			

(b): Model Summary Statistics for CTB Production

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	2.70	0.7390	0.6972	0.6379	253.48	
2FI	2.60	0.8164	0.7197	0.6545	241.85	
Quadratic	1.02	0.9776	0.9567	0.8717	89.81	Suggested
Cubic	0.42	0.9982	0.9925	0.7667	163.35	Aliased

(c): Analysis of Variance (ANOVA) for CTB Production

Source	Sum of Squares	Df	Mean Square	F-Value	P-value; Prob>F
Model	684.44	14	48.89	46.7	<00001
A-Methanol	404.16	1	404.16	386.46	<0.0001
B-Catalyst	14.37	1	14.37	13.74	0.0021
C-Temperature	22.80	1	22.80	21.80	0.0003
D- ReactionTime	76.01	1	76.01	72.67	<0.0001
AB	5.61	1	5.61	5.36	0.0352
AC	5.53	1	5.53	5.29	0.0362
AD	2.81	1	2.81	2.69	0.1217
BC	2.14	1	2.14	2.05	0.1734
BD	12.30	1	12.30	11.76	0.0037

CD	25.78	1	25.78	24.65	0.0002
A ²	3.47	1	3.47	3.32	0.0885
B ²	84.91	1	84.91	81.19	<0.0001
C ²	27.40	1	27.40	26.20	0.0001
D ²	27.40	1	27.40	26.20	0.0001
Residual	15.69	15	1.05		
Lack of fit	15.56	10	1.56	61.29	0.0001
Pure Error	0.13	5	0.025		
<hr/>					
R-Square :0.9776 and Adjusted R-Square:0.9567					

4.4 Response surface plots for CTB production (transesterification)

The predicted vs. actual, perturbation and surface plots were used in this section to describe the trend in CTB production yield when methanol/oil ratio, catalyst, reaction temperature and reaction time are either increased or decreased.

Relationship between Predicted and Actual Response

Figure 8 shows the plot between the predicted and actual CTB response, the linear graph generated by the design expert software indicates agreement between the predicted and actual experimental values.

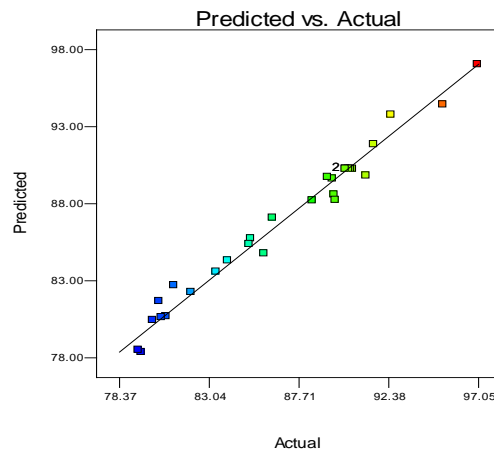


Figure 8: Predicted response versus actual experimental response

Interaction between Catalyst and Methanol/Oil Ratio on CTB Yield

Figure 9 represents a surface contour plot interaction between catalyst concentration and methanol/oil ratio. At a

fixed temperature 50 °C and reaction time of 90 min, the CTB yield of 88.5 % was achieved at a catalyst concentration of 0.80 w % and a methanol/oil ratio range between 7.50-9.00. This result is in agreement with Ngoya *et al.* (2017).

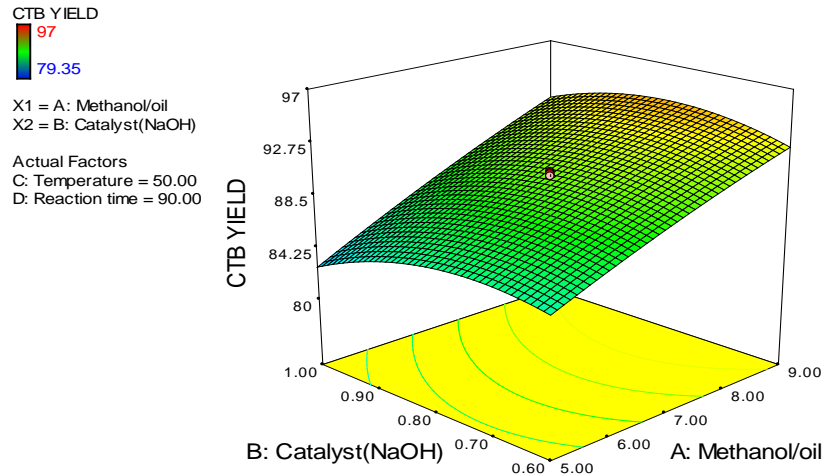


Figure 9: Interaction between Catalyst and Methanol/Oil Ratio

Interaction between Temperature and Methanol/Oil Ratio on CTB Yield

Figure 10 represents a surface contour plot interaction between temperature and methanol/oil ratio. At a

fixed catalyst concentration of 0.80 and reaction time of 90 min, the CTB yield >88.5 % was achieved with a temperature 50 °C and a methanol/oil ratio range between 7.00-9.00.

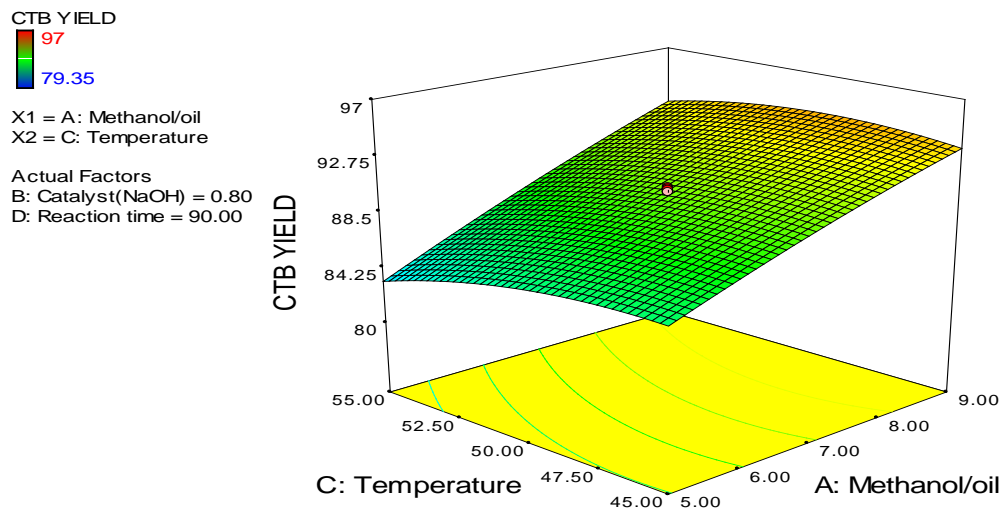


Figure10: Interaction between Temperature and Methanol/Oil Ratio

Interaction between Reaction Time and Methanol/Oil Ratio on CTB Yield

Figure 11 represents a surface contour plot interaction between reaction time and methanol/oil ratio. At a fixed

catalyst concentration of 0.80 w/w and temperature of 50 °C, the CTB yield range of 88.5-92.75 % was obtained using a reaction time of 105 min and methanol/oil ratio of 9.00.

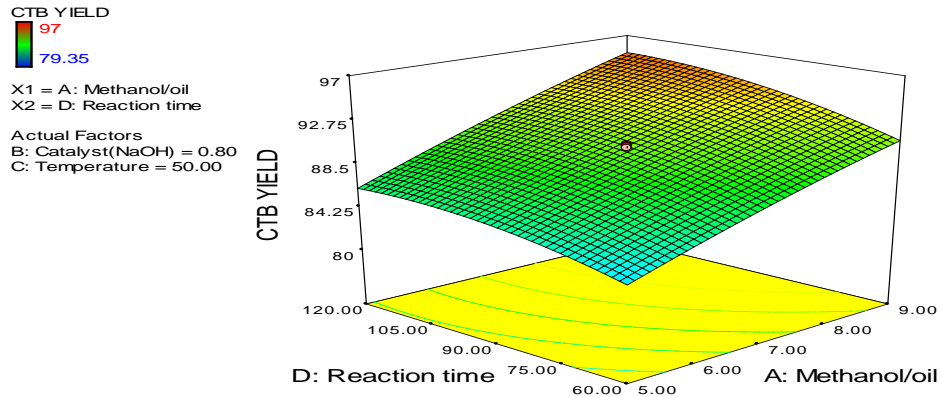


Figure 11: Interaction between Reaction Time and Methanol/Oil Ratio

Interaction between Temperature and Catalyst on CTB Yield

Figure 12 represents a surface contour plot interaction between temperature and catalyst concentration. At a fixed methanol/oil ratio of 7.00 and reaction time of 90 min, the

CTB yield range of 88.5-91 % was recorded at a catalyst range of 0.70-0.80 w %, this indicate that catalyst concentration higher than 0.80 have negative effect on CTB yield.

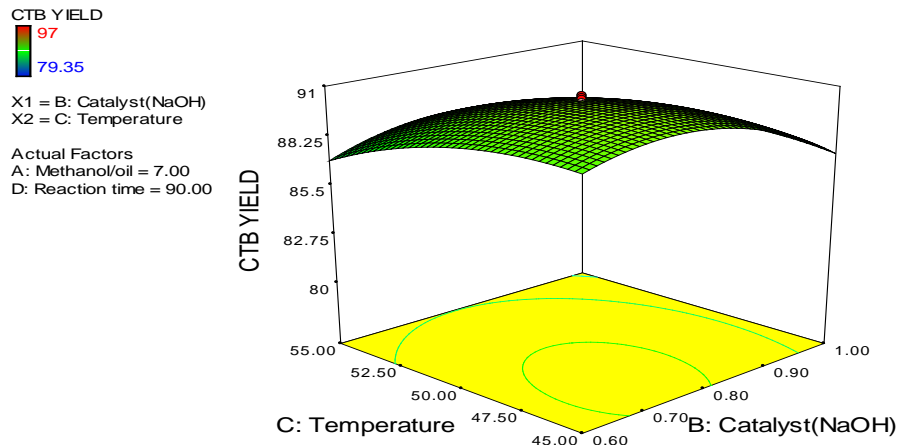


Figure 12: Interaction between Temperature and Catalyst.

Interaction between Independents Variables (A B C and D in coded term) on CTB yield

Figure 13 represents perturbation plot which give the approximate optimum of all the four independent variables as follows; methanol/oil ratio 7:1, catalyst 0.80 w% , temperature 50 °C and reaction time 90 min. The CTB increase with increase in methanol/oil ratio, catalyst, temperature and time till the midpoint is reach, beyond which an increase in methanol/oil ratio increased the CTB yield to within a range of 92.5-97 % and an increase in reaction time also increased CTB yield to within a range of 88-92.5 %. On the other hand, beyond the midpoint CTB yield decreases significantly with

increase in catalyst concentration. This may be due to addition of excessive catalyst that causes more triglyceride to react with the alkali catalyst leading to the formation of soap. Also, beyond the midpoint CTB yield decreases with an increase in temperature. This could be attributed to temperatures close to the boiling point of methanol and the rate of evaporation of methanol was greater than the rate of reaction and that decreases the biodiesel production. Thus, the yield of CTB increases with increase in methanol quantity and time while CTB decrease with increase in catalyst concentration and temperature this result is in agreement with [23].

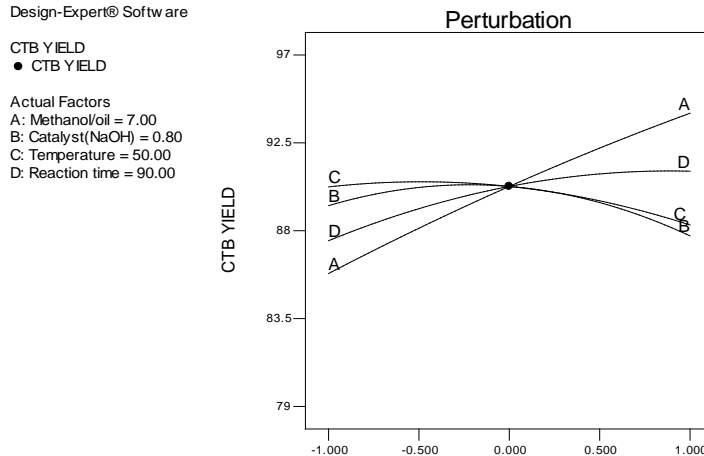


Figure 13: Perturbation Plot of Response Variables on for CTB Yield

4.5 RSM Optimization of both Esterification and Transesterification Stages

The optimized inputs process parameters are methanol/oil ratio (A), catalyst (B), temperature (C) and reaction time (D). The optimal predicted and validated experimental values of FFA reduction are 0.3952 mgKOH/g and 0.40 mgKOH/g respectively while CTB produced has a maximized predicted

and validated experimental values of 95.9 % and 92.4 % respectively as presented in Table 7. The agreement between optimized predicted and validated experimental values indicate reliability of the developed mathematical model equations used in calculating the predicted responses for the two stages in the biodiesel production.

Table 7: Predicted and Validated Experimental Responses from Optimized Input Variables

Process	Optimized values of Process variables				Responses	
	A	B	C	D	Predicted	Experimental
FFA (mgKOH/g)	6	1.60	45	93	0.39529	0.40
CTB (%)	9	0.8	50	120	95.9	92.4

5.0 CONCLUSION

The 2-stage biodiesel production through RSM greatly improved the fuel properties of Cassia tora oil and Cassia tora biodiesel. The CTO was extracted using Soxhlet apparatus and petroleum ether solvent with 8.26 % oil yield. The optimum experimentally validated FFA reduction for

CTO was 0.40 mgKOH/g from initial 2.6 mgKOH/g while the optimum experimentally validated CTB yield was 92.4 %. The model equations obtained can be employed in two-stage cassia *tora* biodiesel production to reduce the fatty acid content of oil and increased biodiesel yield thereby saving time, cost and energy.

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