Synthesis of Biodiesel from *Jatropha curcas* Seed Oil Using CaTiO₃ Catalyst and Optimization of Process Parameters to Improve the Biodiesel Conversation

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ABSTRACT

Biodiesel comprises of monoalkyl esters of long chain fatty acids. It is produced using edible oil, non-edible oil and animal fats by acid or base catalyzed transesterification with ethanol or methanol. In this research, the oil was extracted using n-hexane. Response surface methodology (RSM) with central composite design (CCD) was applied to optimize the biodiesel production from seed oil. An optimum biodiesel yield of 98.50 % was obtained by transesterifying Jatropha seed coil with 0.30 g of catalysts and ethanol to oil molar ratio of 10.50 at 65 °C for 3.68 hrs. The experimental yield is in good agreement with the predicted yield, with relatively small percentage error (0.88 %). This shows that the proposed statistical model is suitable for prediction of optimized biodiesel yield and for optimization of transesterification process.

Introduction

In this climate-sensitive era, a lot of focus has been placed on global warming, environmental degradation, and the rapidly decreasing fossil fuel resources. These have grown to be significant worldwide challenges, and a number of strategies have been proposed to reduce the negative consequences of fossil fuel emissions [1]. The best alternative to diesel fuel, which is regarded to be a clean and renewable fuel, is biodiesel [2-4]. Currently, biodiesel is a less harmful, biodegradable fuel made from renewable sources that is a significant replacement for fossil fuel in a sustainable strategy that takes into account both economic and environmental factors [5-7] In the automobile sector, it is used as a substitute for diesel fuel and is frequently referred to as No. 2 diesel. This biofuel has several advantages over traditional diesel fuel, including a high cetane number, minimal smoke and particles, and low carbon dioxide and hydrocarbon emissions [8]. It lessens smoke, unburned hydrocarbons, and carbon (II) oxide emissions. Vegetable oil, on the other hand, has a high density, a high viscosity, a reduced calorific value, and poor non-volatility, which causes atomization issues, pumping issues, and poor combustion inside a diesel engine's combustion chamber. Vegetable oils used in diesel engines for an extended period of time are likely to cause issues such gumming, injector fouling, piston ring sticking, and contamination of lubricating fluids. The high viscosity of vegetable oils is to blame for all of the aforementioned issues. Therefore, a method must be developed to lower vegetable oil's viscosity to a level that is closer to that of diesel. Solutions to the concerns include preheating the oils, coupling them

with diesel, thermal cracking, and transesterification [9,10]. Long chain fatty acid monoalkyl esters are indeed the crucial constituent of biodiesel. It is synthesized through the transesterification of animal fats, non-edible oils, and edible oils using an acid or base catalyst and ethanol or methanol. A lot of work has been put towards transesterifying oil made from *Jatropha curcas*, soybean, sunflower, cotton seed, rapeseed, and palm oils to produce biodiesel [11]. The experiments used to refine the transesterification of *Jatropha curcas L.* to produce ethanol were covered in this paper. Once seed oil and ethanol are mixed, transesterification is impacted by a number of factors, such as the catalyst, the duration of the reaction, and the molar ratio. Here, utilizing response surface approach and central composite design, our main goal was to better understand the interactions between the independent factors and response in order to find the ideal circumstances for biodiesel synthesis.

Materials and Method
Materials / Equipment
The tools utilized for this experiment include a NYC12 muffle furnace, a Soxhlet extractor setup, a rotary shaker, a water bath (HHW420) from B-scientific in England, a heating mantle, and a reflux condenser (Bio Techno Lab, Mumbai, India)
Chemicals and Reagents

All of the chemicals and reagents utilized in this study were of the analytical grade.

Sample Collection and Preparation
The Department of Biological Sciences at Abubakar Tafawa Balewa University, Bauchi, identified the fresh seeds of *Jatropha curcas* that were obtained from the Railway Quarters in Bauchi, Bauchi State. The samples were cleaned three times with distilled water, dried under cover, and stored for further use.

Soxhlet Extraction
The shells of the *Jatropha curcas* seeds were delicately removed. Oil was extracted from the collected kernels. With a small adjustment, the procedure outlined [12] was employed. The seed kernels were mechanically crushed and defatted in a Soxhlet device. N-hexane was used for the extraction. The procedure was carried out for six hours. By vacuum evaporation and exposure to heat in a drying oven set at 50 °C, the solvent was eliminated. The proportion of total oil in *Jatropha curcas* seed kernels used to calculate the amount of oil recovered.The final value, which is the average of all the separations, was run in triplicate for each extraction. Seed oil that had been extracted was kept in a freezer at -20 °C for upcoming physicochemical tests.

Experimental Design
A central composite design (CCD) and response surface methodology (RSM) approach were used to maximize the generation of biodiesel from seed oil. In this study, the dependent variable was either the yield of fatty acid methyl esters (FAMEs) or biodiesel, and three independent parameters (reaction time, catalyst loading, and methanol to oil molar ratio) were assessed. It was determined the range and levels of the independent variables for the transesterification process [13].

Model Fitting and Statistical Analysism
Version 7.0 of the Design Expert software. Regression analysis was used to fit the equations using the experimental data (STAT-EASE Inc., Minneapolis, USA). The degree of correlation (R^2) was used to assess the effectiveness of the model, and an analysis of variance was used to assess the statistical significance of the equations developed (ANOVA).

Preparation of catalyst $CaTiO_3$ (using CaO from Calcined Egg-shell)
To synthesize the $CaTiO_3$ catalyst, calcined egg shell (CaO) and TiO_2 were crushed in a mortar for 10 to 15 minutes at a molar ratio of 1:1 with 20.0 g $CaCO_3$ and 20.0 g TiO_2. For three hours, the mixture was calcined at 550 °C. and then for 3.5 hours at 1050 °C. to obtain $CaTiO_3$ as a white solid that was preserved in a desiccator and stored in a dry container.

Production of Biodiesel Fuel
Trans-esterification and separation and washing steps were both used during the biodiesel synthesis process.

Trans-Esterification Phase
Glyceride (oil) and alcohol react during the trans-esterification phase in the presence of a catalyst. By transesterifying ethanol with crude *Jatropha curcas* seed oil (triglycerides) in the presence of a $CaTiO_3$ catalyst, biodiesel was created. Response surface approach was used to optimize this process (RSM). The yield was

predicted using a second-order mathematical model as a function of the catalyst concentration, the reaction time, and the ethanol/oil molar ratio.

Table 1: The Levels and Range of Independent Variables of Transesterification Process

Variables	Coding	Unit	-α	-1	0	1	+ α
				Levels			
Catalyst	A	G	0.04	0.10	0.3	0.50	0.64
Molar ratio	B	M	6.95	9	12	15	17.02
Time	C	Hr	0.32	1	2	3	3.68

Table 2: Design matrix of experiments and their respective experimental yield and predicted yield

Run	A: Catalyst(g)	B:molar ratio (M)	C: Time(hr)	Experimental yield (%)	Predicted Yield (%)
1	0.10	9.00	1.00	98.50	98.00
2	0.50	9.00	1.00	98.00	97.00
3	0.10	15.00	1.00	99.00	98.66
4	0.50	15.00	1.00	98.00	98.24
5	0.10	9.00	3.00	97.50	97.54
6	0.50	9.00	3.00	97.00	97.11
7	0.10	15.00	3.00	98.00	98.20
8	0.50	15.00	3.00	98.00	97.78
9	0.04	12.00	2.00	97.90	98.17
10	0.64	12.00	2.00	97.50	97.53
11	0.30	6.95	2.00	97.00	97.33
12	0.30	17.05	2.00	98.50	98.45
13	0.30	12.00	0.32	98.00	98.28
14	0.30	12.00	3.68	97.90	97.50
15	0.30	12.00	2.00	98.00	97.89
16	0.30	12.00	2.00	97.80	97.89
17	0.30	12.00	2.00	97.70	97.89
18	0.30	12.00	2.00	97.70	97.89
19	0.30	12.00	2.00	97.80	97.89
20	0.30	12.00	2.00	97.90	97.89

Table 3: Sequential Model Sum of Square

Source		Sum of square	Degree of freedom	Mean square
Mean	vs	1.916E+005	1	1.916E+005
Total				
Mean	vs	2.80	3	0.93
Total				

2FI vs Linear	0.25	3	0.083		0.1	1.11	15	1.0	99.3806 98.66 0.88
Quadratic vs 2FI	0.12	3	0.040			0.47		0	0.7085
Cubic vs Quadratic	0.79	5	0.16			11.52			0.0090 Aliased
Residual	0.068	5	0.014						
Total	1.916E+005	20							

"Sequential Model Sum of Squares "Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Table 4: Analysis of Varience

Source	Sum of square	Degree of freedom	Mean square	F-value	p-value Prob >F	
Model	2.80	3	0.93	12.17	0.0002	Significant
A-cayalyst	0.57	1	0.57	7.39	0.0152	
B-Molar ratio	1.50	1	1.50	19.54	0.0004	
C-Time	0.73	1	0.73	9.59	0.0069	
Residual	1.23	16	0.077			
Lack f fit	1.16	11	0.11	7.70	0.0177	Significant
Pure error		0.068	5	0.014		
Cor total		4.03	19			

Table 5: Optimization criteria for transesterification process

Factors	Goal	Lower limit	Upper limit
Molar ratio	Minimize	9	15
Time	Minimize	1	3
Catalyst	Minimize	0.1	0.5
Biodiesel	Maximize	97	98.50

Table 6: Result of model validation at the optimum conditions

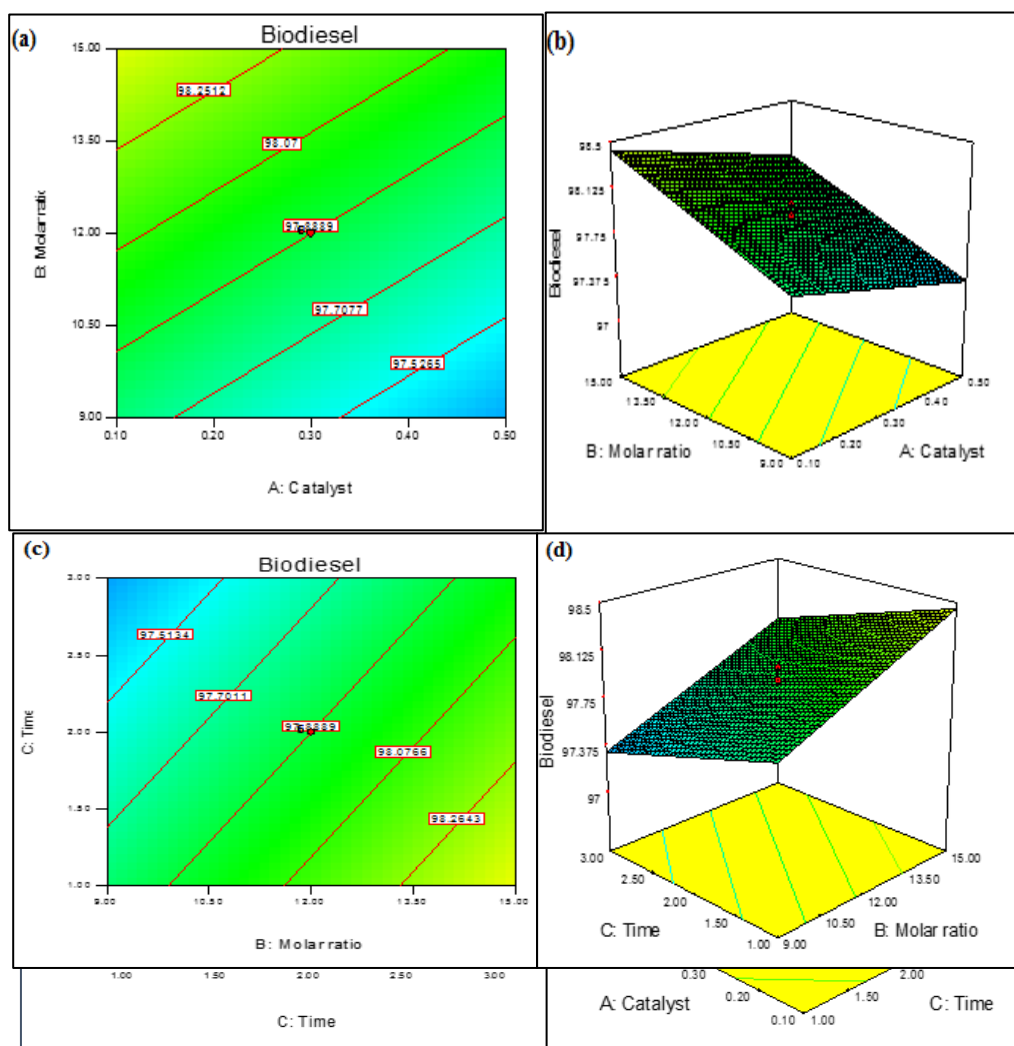| Catalyst (%)	Molar ratio (M)	Time (hr)	Experimental yield (%)	Predicted yield	Percentage error (%)

Figure 1: Counter plot and 3D for experiment

| 850.880 | RHC=CHR | Methylene group |
| 722.350 | R_2CH_2 | Alkenes |

Table 7: Functional groups present in *Jatropha curcas* biodiesel

Wave number (cm^{-1})	Types of vibration	Nature of functional group
3004.280	CH=C-H	Stretching of methyl ester
2922.520	C-H (stretching)	Alkanes
2853.210	C-H (stretching)	Alkanes
1724.140	C=O (stretching)	Esters
1435.320	C-H (bending)	Alkane
1462.140	C-H (bending)	Alkanes
1195.500	C-O (stretching/ bending)	Esters
1169.520	C –O (stretching)	Esters
1016.060	C-O-C antisymmetric	Alcohols, ethers esters

Discussion

20 sets of experiments, including 23 factorial experiments, 6 axial points, and 6 replicas of the center point, were produced for this study.

A mathematical model that links the biodiesel yield to the independent reaction variables using a second-order polynomial equation was created using each response from the transesterification process, as shown below.

$$Y = b_o \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_o x_i^2 + \sum_{i=1}^{n=1} \sum_{j=i+1}^{n} b_o x_i x_j \text{------------1}$$

Where Y is the anticipated biodiesel yield, bo denotes the constant coefficient, bi denotes the linear coefficients, bij denotes the interaction coefficients, bii denotes the quadratic coefficients, and xi denotes the coded values of the experimental variables.

Model Fitting and Statistical Analysis

Version 7.0 of the Design Expert software. Regression analysis was used to fit the equations using the experimental data (STAT-EASE Inc., Minneapolis, USA). The value of the correlation ($R2$) can be used to assess the model's quality, and analysis of variance can be used to assess the statistical significance of the equations created (ANOVA).

Development of regression model

The full experiment design matrix, along with the experimental yield and projected yield, are displayed in Table 2. The yield of biodiesel that was discovered, according to the table, was between 97 and 98.5%.

As seen in Table 3, the RSM program will create a number of models (linear, two-factor interaction (2FI), quadratic, and cubic polynomial) that are best suited to the answer. According to the sequential model sum of square, the linear model's highest order polynomial with relevance of additional terms and the model's lack of aliasing made it the best model to suit the response. The final equation in terms of actual factor for the biodiesel production was calculated below using the equation 2

Biodiesel = +97.34672-06185A+0.11039B-0.23198C-
--2

where the coded terms A, B and C represent catalyst concentration, ethanol to oil molar ratio and reaction time respectively. Positive sign in front of the terms denotes synergic effect while negative sign indicates antagonistic effect [14]. The term A therefore, plays a significant function in improving the biodiesel yield whilst the other terms B and C play significant function in reducing the biodiesel yield.

ANOVA

The linear mode's significance and fitness were assessed using anova. Table 4 displays the ANOVA for the response surface linear model. The model is implied to be significant by the Model F-value of 12.17. A "Model F-Value" this large might happen owing to noise only 0.02% of the time. When "Prob > F" is less than 0.0500, model terms are considered significant. A, B, and C are important model terms in this instance. Model terms are not significant if the value is higher than 0.1000. With a 95% confidence level, the "Lack of Fit F-value" of 7.70 indicates that the Lack of Fit is significant. A "Lack of Fit F-value" this large could only happen owing to noise 1.77% of the time.

Study of parameters

Figures 1a and 1b display the contour plot and the three dimensional (3D) plot for the interaction effect between A: Catalyst and B: molar ratio. The reaction temperature and time were kept constant at 65 ℃ and 2 hrs, respectively, throughout the experiments.

The contour plot Figure 1a shows that higher biodiesel yield (> 98 %) was obtained at high level of molar ratio and low level of catalyst. The 3D respond surface shows that the biodiesel yield increased with increasing molar ratio and decreasing the concentration of catalyst. At 9 molar ratio and 0.30 g catalyst 97.70 % yield was obtained, when the concentration of catalyst increased to 97.53 % conversion was achieved. At 0.10 g of catalyst and 10 molar ratio 97.89 % yield was obtained. Increasing molar ratio from 10 to 13. 98.25 % was obtained. This implies that ethanol has a direct relationship with the biodiesel conversion. Adequate amount ethanol does not leads to difficulty in separation because it decreases the glycerol solubility in product phase. Increasing catalyst concentration beyond 0.10 g, decreased conversion was found due to the meagre diffusion among oil, ethanol and solid catalyst phases while using an inadequate amount of catalyst. This statement was in agreement with what was reported [15].

The contour plot and the three dimensional (3D) plot for the interaction effect between B: molar ratio and C: time was shown in figure 1c and 1d. The reaction temperature and catalyst were kept constant at 65 ℃ and 0.30 g, respectively, throughout the experiment. The contour plot 1c shows that higher biodiesel yield (> 98 %) was obtained at high level of molar ratio (13.22 molar ratio) and at low reaction time (1.00 hr). The 3D respond surface shows that the biodiesel yield was increased with increasing molar ratio and decreasing the reaction time. Decreasing molar ratio from (13.50 to 10) about 97 % biodiesel was obtained. When reaction time was increased to 2 hrs a 97.60 % conversion was achieved. Increasing ethanol increases the biodiesel conversion, this clearly indicates that ethanol has greater impacts on a biodiesel conversion

The contour plot and the three dimensional (3D) plot for the interaction effect between A: catalyst and C: time was shown in figure 1e and 1f. The reaction temperature and molar ratio were kept constant at 65 ℃ and 12 molar ratio respectively, throughout the experiment. The counter plot 1e shows that at a minimum concentration of catalyst and reaction time the highest biodiesel yield was achieved. The 3D respond surface shows that the biodiesel yield increased with decreasing catalyst and decreasing the reaction time. At 1.6 hr and 0.24 g catalyst a 98.19 % biodiesel was obtained. When the catalyst increased to 0.40 g, 90 % was obtained, at 3.00 hrs and 0.50 g catalyst 97.88 % conversion was achieved. This clearly indicated that excess reaction time resulted in decreased the biodiesel yield .

In this research work, biodiesel yield was set to maximum value, while the other reaction parameters

were set in a minimum values as shown in Table 5. The experimental conditions with the highest predicted biodiesel yield were selected for further validation. The result of model validation was shown in Table 6. The optimum biodiesel yield of 98.50 % was obtained by transesterifying Jatropha seed coil with 0.30 g of catalysts and ethanol to oil molar ratio of 10.50 at 65 °C for 3.68 hrs. The experimental yield was in good agreement with the predicted yield, with relatively small percentage error (0.88 %). This indicated that the proposed statistical model was suitable for prediction of optimized biodiesel yield and for optimization of transesterification process.

FT-IR is an important analysis technique which detects the presence and the various characteristic of functional groups present in the oils. The results of FT-IR was shown in Table 8. The peak at 3004.280 cm^{-1} indicates the presence of Stretching of methyl ester CH=C-H. The C-H (stretching) at 2853.210 cm^{-1} to 2922.520 cm^{-1} shows the presence of alkanes. C=O stretching vibration at 1724.140 cm^{-1} indicates the presence of esters. C-H bending vibrations at 1462.140 cm^{-1} shows the presence of alkanes while at 1435.320 cm^{-1} was due to ethyl ester group. C-O bending and stretching at 1195.500 cm^{-1} to 1169.520 cm^{-1} indicate the presence of Alcohols and esters and confirms the biodiesel conversion. RCH=CHR bending at 993.430 cm^{-1} indicates the presence of Alkenes (cis disubstituted alkenes), the presence of $R_2C=CH_2$ Peak at 892.218 cm^{-1} indicates the presence of alkenes. This results agrees with the results C-H stretch (~2900 cm^{-1}), C=O stretch (~1700 cm^{-1}), broad O-H stretch (~3400 cm^{-1}) and C-O stretch (~1100 cm^{-1}) 886 cm^{-1}, 1436 cm^{-1} and 1644 cm^{-1} reported by Snezana *et al.* (2020). 2923.40 cm^{-1} Alkyls (CH_3, CH_2, CH), 1722.68 cm^{-1} ketone, 1598.10 cm^{-1} Alkenes and 1374.83 cm^{-1} Methyl (Ogwuche and Edema, 2020), and also similar to what has been reported by Elkady *et al.* (2015) 721 cm^{-1} -CH_2 rocking, 1373.70 cm^{-1} Bending vibrations of CH_2 groups, 1745 cm^{-1} C=O ester stretch, 1163 cm^{-1} C-O stretching, 1456 cm^{-1} Bending vibrations of the CH_2, 2925 -CH_2 stretching, Latchubugata *et al.* (2018) 1115.85 cm^{-1} for -O-CH_2-C, 1117.75 cm^{-1} for -O-CH_2-C, 1743.87 cm^{-1} for C=O ester 1742.07 cm^{-1} C=O ester, 1160.11 cm^{-1} C-O stretching, 1169.37 cm^{-1} C-O ester, 3005.44 cm^{-1} fore –CH, 2922.24 cm^{-1} for-CH_2, 2922.41 cm^{-1} for -CH_2, 2853.43 cm^{-1} for -CH_2.

4.0 CONCLUSION

In summary, RSM was successfully applied to assess the effects of multiple variables, including the alcohol/oil molar ratio, catalyst concentration and reaction time, for the production of biodiesel from the *Jatropha curcas L.* seed oil. The experimental results suggested the optimal condition as the follows: 0.30 g of catalysts and ethanol to oil molar ratio of 10.50 at 65 °C for 3.68 hrs. This optimized condition was validated with the actual biodiesel yield in 98.50 %. When the catalyst increased to 0.40 g, 90 % was obtained, at 3.00 hrs and 0.50 g catalyst 97.88 %. Since decreasing the biodiesel yield by 0.6 % with the cost of significantly catalyst and reaction time does not appear to be cost-effective, it was suggested that using catalyst mass of 0.30 g for the optimal production of biodiesel from *Jatropha curcas L.* seed oil.

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