



Statistical Optimization of Process Variables for Biodiesel Production from Waste Cooking Oil Using Heterogeneous Base Catalyst

O. A. Aworanti¹, S. E. Agarry^{1*} and A. O. Ajani¹

¹Department of Chemical Engineering, Biochemical Engineering and Biotechnology Laboratory, Ladoké Akintola University of Technology, Ogbomosho, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author OAA designed the study, wrote the protocol and performed the laboratory work. Author SEA managed the literature searches, performed the statistical analysis, wrote the first and revised draft of the manuscript and author AOA managed the analyses of the study. All authors read and approved the final manuscript.

Research Article

Received 28th March 2012
Accepted 23rd November 2012
Published 14th February 2013

ABSTRACT

In this study, the effects of methanol-to-oil molar ratio, catalyst amount and reaction time on the transesterification of waste cooking oil (WCO) to biodiesel were investigated. Methanol with calcium oxide as a heterogeneous catalyst was used for the transesterification process at a temperature of 60°C and 3000 rpm stirring speed. Response surface methodology (RSM) with central composite rotatable design (CCRD) was used at five levels of oil-to-methanol molar ratio (9:1 – 14:1), catalyst (1- 5 %) and reaction time (30 – 90 min) as independent variables and WCO biodiesel yield as dependent variable (response). A statistically significant ($P < 0.0001$) second-order quadratic polynomial regression model with a coefficient of determination, $R^2 = 0.9964$ was obtained for biodiesel production (using Design-Expert Statistical program (v. 6.0.8)) and verification experiment confirmed the validity of the predicted model. Numerical optimization technique based on desirability function was carried out to optimize the WCO conversion to biodiesel. The optimum combinations for transesterification to achieve a predicted maximum biodiesel yield of 94.15 percent were found to be: oil-to-methanol molar ratio, 9.14:1; catalyst amount, 3.49 % and reaction time, 60.49 min. At this optimum condition, the observed biodiesel yield was found to be 94.10 percent. In addition, the fuel

*Corresponding author: Email: sam_agarry@yahoo.com;

properties of the produced biodiesel were in the acceptable ranges according to international standards for biodiesel specifications. The statistical analyses and the closeness of the experimental results to model predictions show the reliability of the regression model and thus, the results will be helpful in selecting an efficient and economical method for biodiesel production from cheap raw materials with high free fatty acid.

Keywords: Biodiesel; transesterification; waste cooking oil; heterogeneous catalyst; methanol; response surface methodology.

1. INTRODUCTION

There is a growing substitution of fossil fuels with fuel derived from renewable resources. Biodiesel is one of such renewable alternative fuel derived from triglycerides by transesterification of vegetable oils and animal fats [1,2]. The advantages of biodiesel fuel over conventional diesel are lower emission pollutants, higher cetane number, no aromatics, no sulphur and contain 10-11% oxygen by weight [3]. In addition, it has higher biodegradability, high flash point and contributes a minimal amount of net green house gases, such as CO₂ and NO_x emissions and sulfur to the atmosphere [4].

Transesterification reactions can be alkali-catalyzed, acid-catalyzed and enzyme-catalyzed. The first two types have received the greatest attention. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems [5]. Transesterification is the reaction of a lipid with an alcohol in the presence of a catalyst to form esters and a by-product, glycerol. The reaction is reversible, and thus an excess of alcohol is usually used to force the equilibrium towards the production of fatty acid esters and glycerol [6,7]. The catalyst used has a determinative effect on the reaction, raising the rate notably. It is known that homogeneous base catalysts such as sodium and potassium hydroxide, carbonates and alkoxides require short times (30 min) to complete the reaction even at room temperature, while homogeneous acid catalysts which include, sulphuric acid require higher temperatures (100°C) and longer reaction times 3 to 4 h [7,8].

Homogeneous catalysts have been found to cause problems such as equipment corrosion and the need for wastewater treatment after removing the dissolved catalyst from biodiesel produced with a large amount of water [9]; side saponification reaction which leads to soap formation, and hence emulsification of biodiesel and glycerol takes place, making it difficult to separate and to purify the biofuel [2,10] and also give rise to increased purification costs, and lower yield in alkali-catalyzed transesterification [11]. These problems can result in increased production costs for biodiesel [12,13]. In order to solve or minimize such problems, catalytic systems using heterogeneous catalyst such as Bronsted bases or Lewis acids, supported alkali, alkali earth oxides, metal oxides and metal complexes have been developed to catalyze the transesterification of vegetable oils with methanol [14,15,16,17].

Heterogeneous catalyst systems are less corrosive, produce no soaps and are easily recovered from the biodiesel products at the end of the reaction and can be reused [18]. Kouzu et al. [19] examined many different types of Ca compounds as transesterification catalysts of soybean oil and waste cooking oil with refluxed methanol. Calcium oxide (CaO) catalyst exhibited the highest transesterification activity among those examined. Thus, CaO has attracted much attention for transesterification reaction since it has high basic strength

and less environmental impact due to its low solubility in organic solvent such as methanol and can be synthesized from cheap sources [20].

It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil [21], which makes it more expensive than pure diesel [22,23]. Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research, especially for those methods concentrating on minimizing the raw material cost. The use of waste cooking oil instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost because it is estimated to be about half the price of virgin oil [24]. In addition, using waste cooking oil could also help to solve the problem of waste oil disposal [25]. Several workers have utilized WCO as feedstock for biodiesel production using homogeneous catalyst [26, 27], however, very few workers have investigated the use of CaO catalyst and WCO in biodiesel production [13,19,26,28].

More also, the process of transesterification is affected by factors such as; the mode of reaction, molar ratio of alcohol- to-oil, type of alcohol, type of oil, nature and amount of catalysts, reaction time, and temperature [6]. The factors can be optimized using statistical optimization method of response surface methodology (RSM). The reaction conditions for pre-treatment and biodiesel production using homogeneous catalyst have been optimized using RSM by many authors [29,30,31]. However, there are little or no data on optimization of reaction conditions for biodiesel production from waste cooking oil using heterogeneous catalyst. The objective of this study is to investigate the effects of process variables (methanol-to-oil molar ratio, catalyst amount and reaction time) on the transesterification of waste cooking oil (WCO) to biodiesel (fatty acid methyl ester) and to optimize the variables using response surface methodology (RSM) with central composite rotatable design (CCRD). Transesterification was performed using CaO as a solid heterogeneous base catalyst.

2. MATERIALS AND METHODS

2.1 Materials

Waste Cooking Oil (WCO) was obtained from a local restaurant in Ogbomoso, Nigeria. The WCO was filtered to remove impurities. Methanol, ferric sulfate, CaO, anhydrous sodium sulfate and other chemicals were obtained from a chemical store in Lagos, Nigeria, and they are of analytical reagent grade. Before being used as a catalyst, CaO was calcined in a muffle furnace at 900°C for 1.5 h under N₂ atmosphere since CaO catalyst is poisoned very fast by atmospheric water and CO₂ [28]. Calcinations' treatment can remove the surface carbonate and hydroxyl groups and improve transesterification reaction rate [32]. The acid and saponification values of the oil were determined using standard titration methods [33] and the procedure described by Gryglewicz [34].

The molecular weight of the oil was determined from the saponification and acid values using Eq. (1) [35]:

$$M = \frac{56.1 \times 1000 \times 3}{SV - AV} \quad (1)$$

Where *SV* and *AV* are the saponification and acid values (mg KOH/g oil), respectively. Water content in the oil was determined using a Karl-Fisher moisture titrator (MKC-610,

Kyoto Electronic Manufacturing Co. Ltd). Density and viscosity measurements were made according to ASTM standards D1298 and D 445 respectively. Density at 15°C was measured using a densimeter. Dynamic viscosity at 40°C was measured using a Bookfield viscosimeter. Kinematic viscosity was estimated using the density at 40°C and the dynamic viscosity. The pour and flash points were determined following ASTM standard D97, D25100-8 and D56, respectively. The properties of WCO are summarized in Table 1. It is seen that the WCO has an acid value of 3.2 mgKOH/g and this corresponds to a free fatty acid value of 1.6 %.

The free fatty acid profile or composition of the oil was analyzed by Trace GC Ultra gas chromatograph (Thermo Electron Corporation, USA) equipped with a flame ionization detection system. The column was Agilent DB-WAX (30 m length, 0.25 mm inner diameter, and 0.25 μ m film thicknesses). The temperature program was as follows: 180°C for 2 min, 8°C/min up to 240°C, and holding time of 8 min. Nitrogen was used as a carrier at a flow rate of 1.0 ml/ min. A sample volume of 1.0 μ l was injected using a split ratio of 1:80. The free fatty acid composition of WCO is presented in Table 2. Table 2 shows that the WCO consists mainly of palmitic, stearic and oleic free fatty acids.

Table 1. Physico-chemical properties of waste cooking oil (WCO)

Parameters	Value
Viscosity at 40°C (mm ² /s)	47.66
Density (kg/m ³) at 15°C	903
Flash point (°C)	310
Free fatty acid (%)	1.6
Acid number (mg KOH/g Oil)	3.2
Saponification value (mg KOH/ g Oil)	182
Water content (%)	0.60

Table 2. Fatty acid composition of waste cooking oil (WCO)

Component	Name	Peak number	Retention time (min)	Composition (%)
C6:0	Caproic	2	9.850	5.840
C14:0	Myristic	8	28.533	0.640
C16:0	Palmitic	12	35.700	33.41
C18:0	Stearic	16	41.633	21.66
C18:1 trans/cis	Oleic	17	42.416	21.46
C18:2	Linoleic	19	43.466	10.37
C18:3	Linolenic	22	44.666	0.293
C20:1_C18:3	Eicosenoic	23	45.450	0.140
C24:1	Lignoceric	36	55.016	1.880

2.2 Solid Base- Catalyzed Transesterification of WCO

The method of Alamu et al. [36] was used for the transesterification process. A measured amount of methanol and calcium oxide (CaO) was poured into a beaker and the mixture was stirred by a magnetic stirrer for 10 minutes after which it was preheated to about 60°C below the boiling point of methanol. Thereafter, 200 ml of WCO was taken and heated to 60°C on a temperature water bath before it was poured into a blender. The agitated mixture of

methanol and CaO was then poured gently into the WCO in the blender (Dry and wet mill blender 462, Nakai, Japan). The blender lid was tightly secured and then switched on. The entire content was allowed to blend for the required reaction time before the blender was switched off. After the whole reaction, the reaction product was then decanted from the blender and centrifuge at 6000 rpm for 20 minutes, where the CaO catalyst was separated from the reaction product.

Then the supernatant product mixture was exposed to open air for 30 minutes to evaporate excess methanol. Thereafter, it was poured into a separating funnel and allowed to settle overnight so as to separate the glycerin from the biodiesel. The lower glycerin layer was drawn off and the upper biodiesel layer was then removed, dried and weighed. The biodiesel (FAME) yield of the transesterification process was calculated using Eq. (2) given by Leung and Guo [37]:

$$\text{Biodiesel (FAME) Yield (\%)} = \frac{\text{Mass of biodiesel (FAME) produced}}{\text{Mass of WCO used}} \times 100 \quad (2)$$

2.3 Statistical Experimental Design for Optimization of Biodiesel Production

After approximation of the best conditions by “one-factor-at-a time” method; RSM was used to investigate the influence of methanol-to-oil molar ratio, catalyst amount and reaction time on the conversion of WCO to biodiesel. A five-level-three-factor central composite rotatable design (CCRD) was employed in the optimization study, requiring 20 experiments. The methanol-to-oil molar ratio, catalyst concentration and reaction time were the independent variables selected to optimize the conditions for biodiesel (fatty acid methyl ester) production of CaO catalyzed transesterification.

Table 3 gives the factors and their values. Table 4 describes the experimental design and the 20 experiments that were carried out. Experimental runs were randomized to minimize the effects of unexpected variability in the observed responses. This methodology allows for the formulation of a second-order polynomial equation that describes the process. The conversion of biodiesel was analyzed by the multiple regressions through the least squares method to fit the following Eq. (3):

$$Y = \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (3)$$

Where β_o is the value of the fixed response at the centre point of the design; $\beta_1, \beta_2, \beta_3$ are linear coefficients; $\beta_{11}, \beta_{22}, \beta_{33}$ are quadratic coefficients; $\beta_{12}, \beta_{13}, \beta_{23}$ are the interaction effect coefficients regression terms, respectively; A, B and C are the levels of independent variables. Using the above model, the Design-Expert program (version 6.08) software was used for regression analysis of experimental data and to plot response surface.

Table 3. Experimental range and levels of the independent variables

Factor coding	- α	-1	0	+1	+ α
A (Methanol-to-oil molar ratio)	4:1	6:1	9:1	12:1	14:1
B (CaO catalyst amount, %)	1.6	3	5	7	8.4
C (Reaction time, h)	1	2	3	4	5

Table 4. The central composite design for optimizing CaO-catalyzed transesterification

Run	Coded factor			Actual factors			Biodiesel Yield (%)	
	A	B	C	Molar ratio	Catalyst %	Reaction time	Experimental	Predicted
1	-1	-1	-1	6:1	3	2	75.10	73.94
2	+1	-1	-1	12:1	3	2	77.10	76.48
3	-1	+1	-1	6:1	7	2	80.00	79.76
4	+1	+1	-1	12:1	7	2	87.40	87.00
5	-1	-1	+1	6:1	3	4	85.70	86.01
6	+1	-1	+1	12:1	3	4	83.50	83.70
7	-1	+1	+1	6:1	7	4	77.80	78.38
8	+1	+1	+1	12:1	7	4	79.70	80.77
9	-1.682	0	0	4:1	5	3	65.90	66.15
10	+1.682	0	0	14:1	5	3	70.50	70.30
11	0	-1.682	0	9:1	1.6	3	88.80	89.51
12	0	+1.682	0	9:1	8.4	3	92.60	91.95
13	0	0	-1.682	9:1	5	1	81.70	83.12
14	0	0	+1.682	9:1	5	5	89.40	88.04
15	0	0	0	9:1	5	3	94.00	94.00
16	0	0	0	9:1	5	3	94.00	94.00
17	0	0	0	9:1	5	3	94.00	94.00
18	0	0	0	9:1	5	3	94.00	94.00
19	0	0	0	9:1	5	3	94.00	94.00
20	0	0	0	9:1	5	3	94.00	94.00

3. RESULTS AND DISCUSSION

3.1 Second-Order Quadratic Polynomial Regression Model and Statistical Analysis

Based on the central composite design and results of experiments (Table 4), the quadratic regression model (based on the coded factors) of the experimental data was given as:

$$Y = 94 + 1.19A + 0.68B + 1.42C - 9.1A^2 - 1.14B^2 - 2.96C^2 + 1.25AB - 1.14AC - 3.29BC \quad (4)$$

Where Y was the biodiesel yield (%), A is the methanol-to-oil molar ratio, B the catalyst amount (%), and C the reaction time (min), respectively. The statistical significance of the

model equation was evaluated by the F-value for analysis of variance (ANOVA), which showed that the regression is statistically significant at 95% confidence level. The model F-value of 154.94 for biodiesel production implied that the model was statistically significant (Table 5). There is only a 0.01 per cent chance that a model F-value, this large could occur due to noise alone.

The low probability value (<0.0001) indicates that the model is significant. The correlation coefficient ($R^2 = 0.9929$), adjusted R-squared (0.9865) and predicted R-squared (0.9484) values being a measure of goodness of fit to the model indicates a high degree of correlation between the observed value and predicted values. The coefficient of determination value ($R = 0.9964$), suggests that more than 99.64 per cent of the variance is attributable to the variables and indicated a high significance of the model. Thus, 0.36 per cent of the total variance cannot be explained by the model. The fitted model is considered adequate if the F-test is significant ($P < 0.05$). The analysis of variances (ANOVA) quadratic regression model demonstrated that the model was highly significant, as was evident from the very low probability ($P < 0.0001$) of the F -test and insignificant result from the Lack of Fit model.

The Lack of Fit test is performed by comparing the variability of the current model residuals to the variability between observations at replicate settings of the factors. The Lack of Fit F -value of 2.03 implies the Lack of Fit is not significant relative to the pure error. The Lack of Fit is designed to determine whether the selected model is adequate to describe the observed data, or whether a more complicated model should be used. The Predicted R-Squared value of 0.9484 is in reasonable agreement with the Adjusted R-Squared value of 0.9865. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 38.906 obtained in this research indicates an adequate signal. This model can be used to navigate the design space. The coefficient of the model (parameter estimation) and the corresponding P-values (Values of "Prob > F") are presented in Table 6. The significance of regression coefficients was considered, ignoring those with an insignificant effect on the response at a significance level of 95 per cent.

The P-values of the regression coefficients suggest that among the test variables, linear, quadratic and interaction effects of A (methanol-to-oil molar ratio), B (catalyst amount) and C (reaction time) are highly significant. In this study, A, B, C, A^2 , B^2 , C^2 , AB, AC and BC are significant model terms. Thus, statistical analysis of all the experimental data showed that methanol-to-oil molar ratio, catalyst amount and reaction time had a significant effect on biodiesel yield during the study. Moreover, it is observed that reaction time exerted more pronounced linear effect (higher coefficient values) on biodiesel yield. That is, WCO biodiesel production was mostly and positively influenced by reaction time followed by methanol-to-oil molar ratio and CaO catalyst amount. The quadratic effect of the independent variables on conversion of WCO to biodiesel was significant but negative Fig. 1 shows the predicted versus actual plot of WCO biodiesel yield. Actual values were determined for a particular run, and the predicted values were calculated from the approximating function used for the model.

Table 5. Analysis of variance (ANOVA) for the quadratic response surface model

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob>F
Model	1416.54	9	157.39	154.93	<0.0001
Residual:					
Lack of fit	10.16	5	2.03		
Pure Error	0.000	5	0.000		
Correlation Total	1426.70	19			

$R^2 = 0.9929$; Adj $R^2 = 0.9865$;
Pred $R^2 = 0.94886$

Table 6. Coefficient of the model for the WCO Biodiesel Yield

Factor	Coefficient estimate	Standard error	F-value	P-value	Remarks
Intercept	94.00	0.41	154.93	<0.0001	Significant
A-Molar ratio	1.19	0.27	19.02	0.0014	Significant
B-Catalyst	0.68	0.27	6.21	0.0319	Significant
C- Time	1.42	0.27	27.01	0.0004	Significant
A ²	-9.10	0.27	1173.75	<0.0001	Significant
B ²	-1.14	0.27	18.42	0.0016	Significant
C ²	-2.96	0.27	124.32	<0.0001	Significant
AB	1.25	0.36	12.33	0.0056	Significant
AC	-1.14	0.36	10.21	0.0096	Significant
BC	-3.29	0.36	85.17	<0.0001	Significant

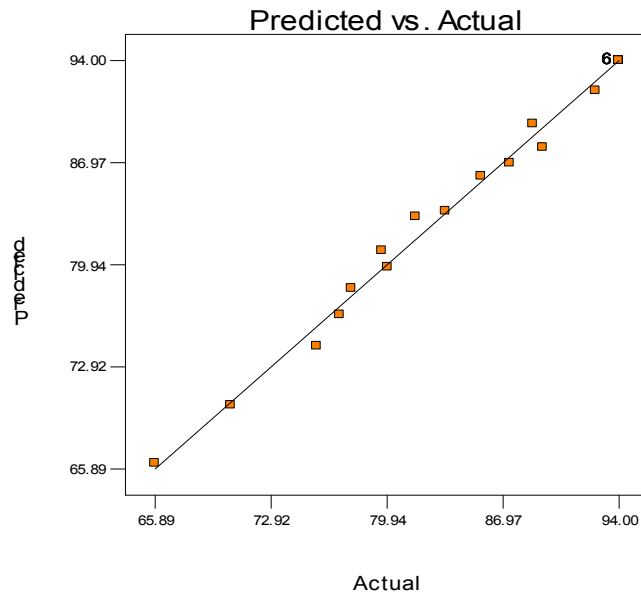


Fig. 1. Predicted versus actual yield of biodiesel

3.2 Effect of Transesterification Process Variables

Based on the analysis of variance, the transesterification reaction was significantly affected by various interactions between the process variables. On the other hand, significant individual process variables that affect the transesterification reaction is methanol-to oil molar ratio (A), catalyst (B), and reaction time (C). The ratio of methanol to oil is one of the important factors that affect the conversion of triglyceride to fatty acid methyl ester (FAME). The results obtained in this study as revealed in Fig. 2, showed that biodiesel yield increased as methanol-to-oil molar ratio increases up till an optimum value after which it decreased. Higher ratio of methanol used could also minimize the contact of excess triglyceride molecules on the catalyst's active sites which could decrease the catalyst activity. Besides that, an increase in the ratio of methanol could also lead to the increase in the purity of the biodiesel layer which would also be responsible for the observed increased in biodiesel yield.

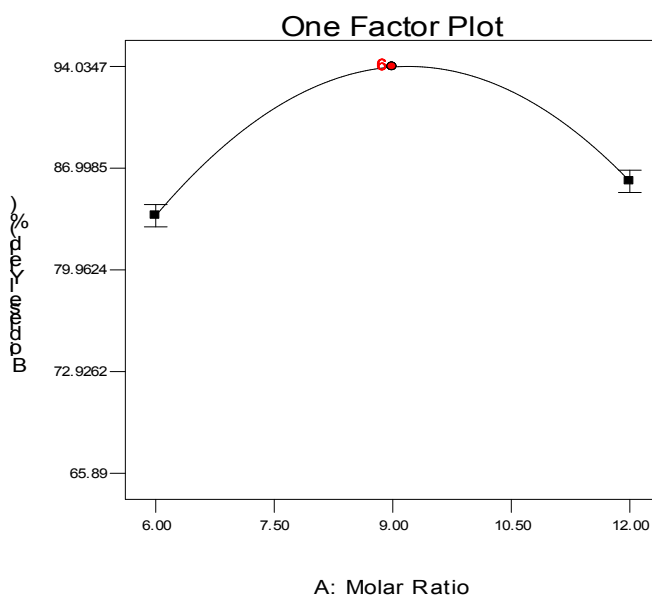


Fig. 2. Effect of methanol-to-oil molar ratio on WCO biodiesel yield

Fig. 3 illustrates effect of the amount (mass) of CaO catalyst on biodiesel yield. When the mass of catalyst was increased from 1 % to 5 %, the active sites of the solid catalyst was increased; accelerating transesterification reaction thereby increasing biodiesel yield. However, maximum biodiesel yield was obtained at a mass of 3 % catalyst.

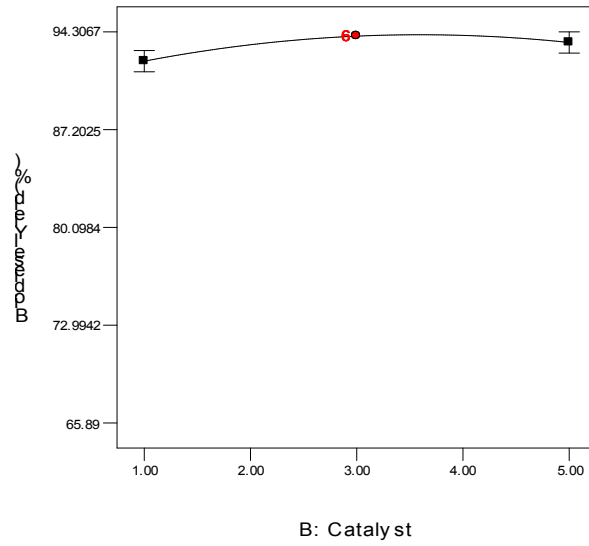


Fig. 3. Effect of amount of catalyst on WCO biodiesel yield

The effect of reaction time on biodiesel yield is shown in Fig. 4. It is seen from the one factor plot that the yield of biodiesel increased with increase in reaction time from 30 to 60 minutes. Above 60 minutes, the biodiesel yield slightly decreased. Therefore, maximum biodiesel yield was obtained at a reaction time of 60 minutes.

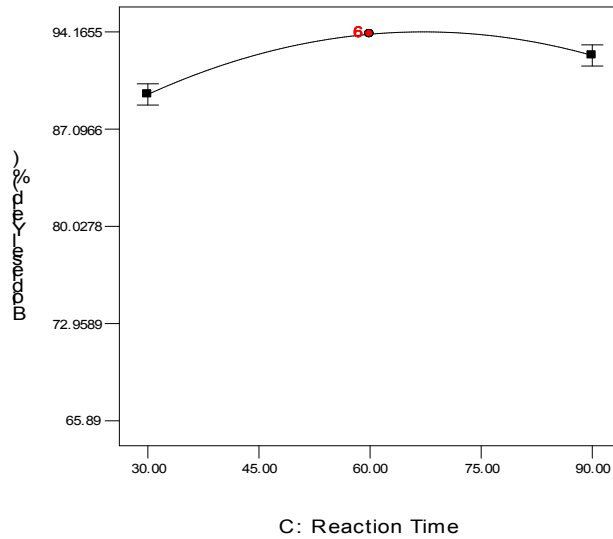


Fig. 4. Effect of reaction time on WCO biodiesel yield

3.3 Effect of Interaction between Process Variables

Three-dimensional response surfaces were plotted on the basis of the model equation to investigate the interaction among the variables and to determine the optimum condition of each factor for maximum CaO-catalyzed transesterification for biodiesel production. The effect of methanol-to-oil molar ratio and catalyst amount on biodiesel production at a constant reaction time of 60 min is presented in Fig. 5. At lower methanol-to-oil molar ratio, the conversion to biodiesel increased with increase in catalyst amount. It seemed that increase in methanol-to-oil molar ratio had significant effect on the conversion to biodiesel at different catalyst amounts. This could be due to the fact that methanol-to-oil molar ratio has a higher coefficient value and a lower p value than catalyst (Table 6). The elliptical nature of the contour plot between the methanol-to-oil molar ratio and catalyst amount indicated that interaction between these two variables had a positive significant effect on the conversion to biodiesel.

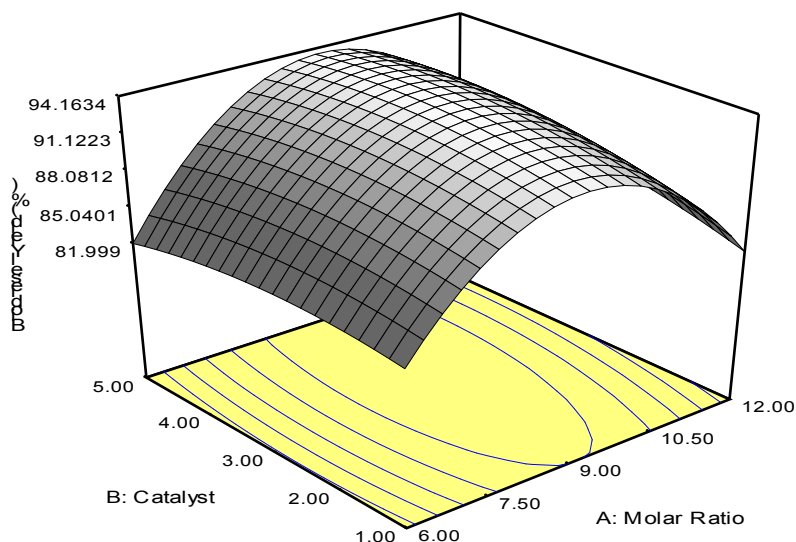


Fig. 5. Response surface plot of the interaction effect of methanol-to-oil molar ratio and catalyst amount on WCO biodiesel yield when the reaction time is 60 minutes

Fig. 6 shows effect of interaction of methanol-to-oil molar ratio and reaction time on conversion of WCO to biodiesel at a constant amount of catalyst amount (3%). There was a high significant effect of reaction time on CaO-catalyzed transesterification. Under such conditions, methanol-to-oil molar ratio of about 9:1 gave the best conversion to biodiesel. In addition, there was negative significant interaction between methanol-to-oil molar ratio and reaction time. This indicates that the CaO biodiesel yield increased with increase in methanol-to-oil molar ratio up till an optimum value (9:1) as reaction time increases; above the optimum value the yield decreased.

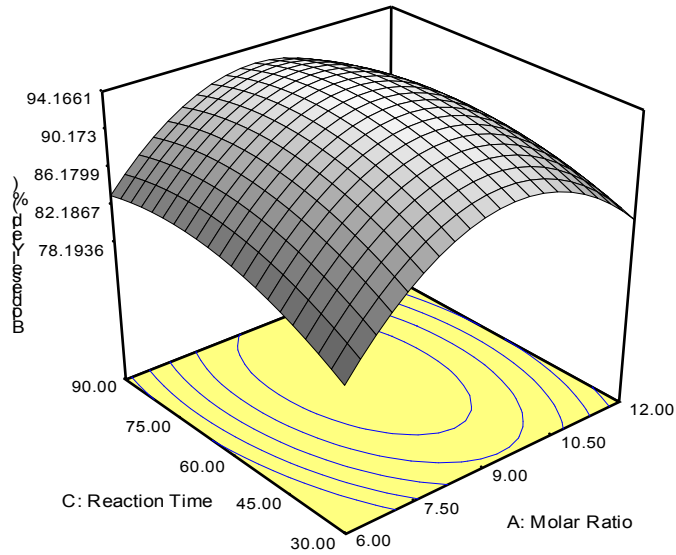


Fig. 6. Response surface plot of the interaction effect of methanol-to-oil molar ratio and reaction time on WCO biodiesel yield when the amount of catalyst is 3 percent

The interaction effect of catalyst amount and reaction time on WCO biodiesel production at a constant methanol to-oil molar ratio of 9:1 is shown in Fig. 7. The biodiesel production was influenced significantly by catalyst amount and reaction time and the optimal catalyst amount was around 3% with methanol-to-oil molar ratio 9:1 and reaction time 60 min. There was a negative significant interaction between catalyst amount and reaction time. This showed that the CaO biodiesel yield reduces with increase in catalyst and reaction time above the optimum value of 60 minutes.

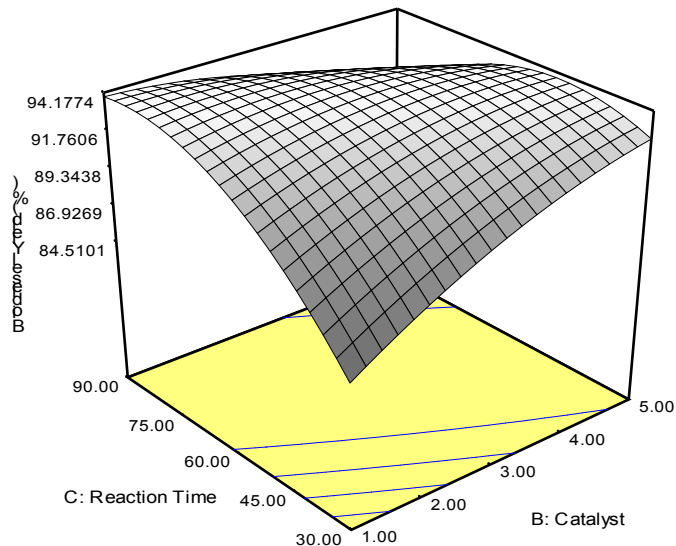


Fig. 7. Response surface plot of the interaction effect of catalyst amount and reaction time on WCO biodiesel yield when the molar ratio of methanol to oil is 9:1

3.4 Optimization and Validation

Numerical optimization technique based on desirability function was carried out to determine the workable optimum conditions for the conversion of WCO to biodiesel (FAME). In order to provide an ideal case for biodiesel production, the goal for methanol-to-oil molar ratio, catalyst amount and reaction time was set in range based upon the requirements of the WCO conversion and biodiesel yield was set on maximize. The predicted optimum (uncoded) values of methanol-to-oil molar ratio, catalyst amount and reaction time were found to be 9.14:1, 3.49 % and 60.49 min, respectively, to achieve 94.15 % maximum WCO biodiesel yield; while desirability was 1.00 for the experiment (Fig. 8).

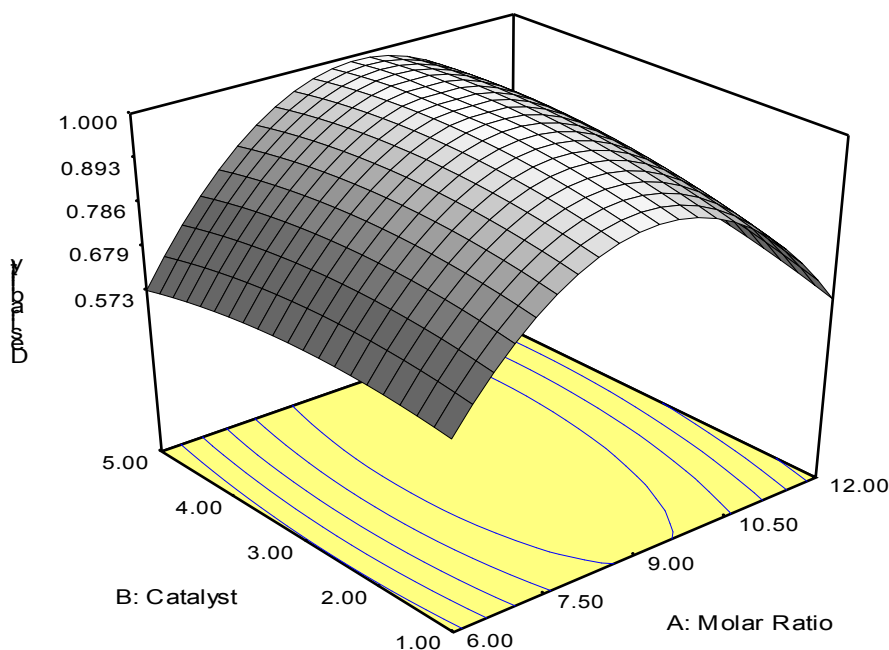


Fig. 8. Desirability plot to optimize the conversion of WCO to biodiesel

Nevertheless, validation experiment was conducted to determine the optimum WCO biodiesel yield when the process variables were set at the favourable predicted optimum levels established above, through CCRD and RSM. The per cent error was investigated for validation of experiments. Errors between predicted and actual values were calculated according to Eq. (5).

$$\text{Error} = \frac{(\text{Actual Value} - \text{Predicted Value}) \times 100}{\text{Actual Value}} \quad (5)$$

In the optimized condition for conversion of WCO to biodiesel, 94.10 % biodiesel (FAME) yield was obtained from the validation experiment. The percentage error between the predicted and actual values was found to be -0.05. The results clearly indicated that no significant difference was observed. As can be seen in Table 4 in the un-optimized condition the highest WCO biodiesel yield was 94 %, while in the optimized condition the highest biodiesel yield is 94.10%. The results clearly indicated the effectiveness of process variables

optimization in biodiesel production. A full factorial experimental design using Box-Behnken design (BBD) was performed by Zhang et al. [28] and Charoenchaitrakool and Thienmethangkoon [38] to assess the effects of three variables on biodiesel yield from *Zanthoxylum bungeanum* seed oil (ZSO) and waste frying oil, respectively. Zhang and co-workers [28] obtained high conversion of ZSO to biodiesel in which the yield was around 96 % and the determined optimum experimental conditions were methanol-to-oil ratio, 11.69:1, CaO catalyst amount, 2.52% and reaction time of 2.45 h. While Charoenchaitrakool and Thienmethangkoon [38] achieved a maximum percentage FAME yield of 90.56 % at a determined optimum reaction conditions of methanol to oil molar ratio of 6.1:1, 0.68 % sulfuric acid and 51°C with a reaction time of 60 min in the first step, followed by using molar ratio of methanol to product from the first step of 9.1:1, 1% KOH and 55°C with a reaction time of 60 min in the second step. Wang and co-workers [39] used a central composite design to investigate the optimal conditions for biodiesel production from trap grease with 50 % free fatty acid. The highest methyl ester content of 89.67 % was obtained when methanol to oil molar ratio of 35:1, 11.27 wt % H₂SO₄, 95°C and reaction time of 4.59 h were used. Also, Encinar et al. [40] reported that for the biodiesel production from waste frying oil, 94.2 % maximum FAME yield was achieved when a methanol to oil molar ratio of 6:1, 1 wt. % KOH, and 65°C with the reaction time of 2 h were used as reaction conditions.

3.5 Physical Property of Biodiesel Produced

In the previous section, the optimal conditions for biodiesel produced were found to be as follows: methanol to oil molar ratio of 9.14:1, 3.49 % of CaO and 60.49 min of reaction time. The biodiesel (FAME) obtained from the optimum conditions was 94.10 %. The biodiesel produced from this condition was further analyzed to determine its viscosity, density, pour point and cloud point based on the ASTM standards. Table 7 shows the physical property of the produced biodiesel. Even though the % biodiesel (FAME) yield obtained in this study was lower than 96.50 %, some physical properties of the product including viscosity, density, acid value, pour point and flash point complied with the ASTM D6751-02 and EN 14214 standard.

Table 7. Properties of biodiesel produced from WCO

Properties	WCO biodiesel	EN14214	ASTM D – 6751
Acid value	0.35	-	< 0.8
Density at 32°C (Kg/m ³)	893	860 – 900	875 – 900
Kinematic viscosity at 40°C (mm ² /s)	4.10	3.5 – 5.0	1.9 – 6.0
Pour point (°C)	- 8	-	- 15 to 10
Flash point (°C)	162	-	> 130
Biodiesel yield (%)	94.10	> 96.5	> 96.5

4. CONCLUSION

Transesterification of WCO using CaO as a catalyst was optimized by RSM, and the optimal conditions of the variables were as follows: methanol-to-oil molar ratio 9.14:1, catalyst amount 3.49 %, and reaction time 60.49 min. Under optimal conditions, the conversion to biodiesel reached above 90 percent. Methanol-to-oil molar ratio, catalyst amount and reaction time had a significant effect on biodiesel yield. WCO biodiesel production was mostly and positively influenced by reaction time followed by methanol-to-oil molar ratio and

CaO catalyst amount. Interactions between methanol-to-oil molar ratio and CaO catalyst had a positive significant effect on the conversion of WCO to biodiesel. While interactions between methanol-to-oil molar ratio and reaction time and interactions between CaO catalyst amount and reaction time had negative significant effects on WCO conversion. The results supported that waste vegetable oil with high FFA can be used for biodiesel production by solid alkali-catalyzed transesterification as well as the possibility of CaO after calcinations being used as an effective heterogeneous alkaline catalyst for biodiesel production.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Nie K, Xie F, Wang F, Tan T. Lipase catalyzed methanolysis to produce biodiesel optimization of the biodiesel production. *J. Mol. Catalysis B: Enzymatic*. 2006;43:142-147.
2. Shibasaki-Kitakawa N, Honda H, Kuribayashi H, Toda T, Fukumura T, Yonemoto T. Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst. *Bioresour. Technol.* 2007;98:416-421.
3. Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresour. Technol.* 2007;98:183-190.
4. Bouaida A, Martinez M, Aracil J. Long storage stability of biodiesel from vegetable and 414 used frying oils. *Fuel*. 2007;86:2596-2602.
5. Watanabe Y, Shimada Y, Sugihara A, Tominaga Y. Enzymatic conversion of waste edible oil to biodiesel fuel in a fixedbed bioreactor. *J. Am. Oil Soc. Chem.* 2001;78(2):703-707.
6. Zhang Y, Dube MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment, *Bioresour. Technol.* 2003;89:1-6.
7. Meher LC, Vidya Sagar D, Nail SN. Technical aspects of biodiesel production by transesterification-a review, *Renew. Sustain. Energy Rev.* 2006;10:248-268.
8. Guan G, Kusakabe K, Yamasaki S. Tri-potassium phosphate as a solid catalyst for biodiesel production from waste cooking oil. *Fuel Process. Technol.* 2009;90:520-524.
9. Vicente G, Martinez M, Aracil J. Integrated biodiesel production: A comparison of different homogeneous catalysts systems. *Bioresour. Technol.* 2004;92:297-305.
10. Xie W, Peng H, Chen L. Transesterification of soybean oil catalyzed by potassium 611 loaded on alumina as a solid-base catalyst, *Appl. Catal. A.*, 2006;300:67-74.
11. Shu Q, Yang B, Yuan H, Qing S, Zhu G. Synthesis of biodiesel from soybean oil and methanol catalyzed by zeolite beta modified with La³⁺. *Catal Commun.* 2007;8:159-5.
12. Ebiura T, Echizen T, Ishikawa A, Murai K, Baba, T. Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid-base catalyst. *Applied Catal. A: Gen.* 2005;283:111-116.
13. Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*. 2008;87:216-221.
14. Kouzu M, Umemoto M, Kasuno T, Tajika M, Aihara Y, Sugimoto Y, Hidaka J. Biodiesel production from soybean oil using calcium oxide as a heterogeneous catalyst. *J. Jpn. Inst. Energy.* 2006;85:135-141.
15. Babu NS, Sree R, Prasad PSS, Lingaiah N. Room-temperature transesterification of edible and non-edible oils using a heterogeneous strong basic Mg/La catalyst. *Energy Fuels.* 2008;22:1965-1971.

16. Yan S, Lu H, Liang B. Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production. *Energy Fuels*. 2008;22:646-651.
17. Noiroj K, Intarapong P, Luengnaruemitchai A, Jai-In S. A comparative study of KOH/Al₂O₃ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. *J. Renewable Energy*. 2009;34:1145-1150.
18. Kim HJ, Kang BS, Kim MJ, Park YM, Kim DK, Lee JS, Lee KY. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*. 2004;93-95:315-320.
19. Kouzu M, Kasuno T, Tajika M, Yamanaka S, Hidaka J. Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Appl. Catal. A: Gen.* 2008;334:357-365.
20. Zabeti M, Wan Daud WMA, Aroua MK. Activity of solid catalysts for biodiesel production: a review. *Fuel Process Technol.* 2009;90:770-777.
21. Connemann J, Fischer J. Biodiesel in Europe 1998: Biodiesel processing technologies. Paper presented at the International Liquid Biofuels Congress, Brazil. 1998:15.
22. Loreto E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin Jr, JG. Synthesis of biodiesel via acid catalyst. *Ind. Eng. Chem. Res.* 2005;44:5353-5363.
23. Marchetti JM, Miguel VU, Errazu AF. Heterogeneous esterification of oil with high amount of free fatty acid. *Fuel*, 2007;86:906-910.
24. Supple B, Howard-Hildige R, Gonzalez-Gomez E, Leahy JJ. The effect of steam treating waste cooking oil on the yield of methyl ester. *J. Am. Oil Soc. Chem.* 1999;79(2):175-178.
25. Wiltsee G. Waste grease resource in 30 US metropolitan areas. In: *The Proceedings of Bioenergy 98 Conference, Wisconsin*, 1998:956-963.
26. Son SM, Kusakabe K, Guan G. Biodiesel synthesis and properties from sunflower and waste cooking oils using CaO Catalyst under reflux conditions. *J. Appl. Sci.* 2010;10:3191-3198.
27. Patil PD, Gude VG, Reddy HK, Muppaneni T, Deng S. Biodiesel Production from Waste cooking oil using sulfuric acid and microwave irradiation processes. *J. Environ. Protect.* 2012;3:107-113.
28. Zhang J, Chen S, Yang, R, Yan, Y. Biodiesel production from vegetable oil using heterogeneous acid and alkali catalyst. *Fuel*. 2010;89:2939-2944.
29. Ghadge SV, Raheman H. Process optimization for biodiesel production from Mahua (*Madhuca indica*) oil using response surface methodology. *Bioresour Technol.* 2006;97:379-84.
30. Yuan X, Liu J, Zeng G, Shi J, Tong J, Huang G. Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. *Renew Energy*. 2008;33:1678-84.
31. Jeong GT, Yang HS, Park DH. Optimization of transesterification of animal fat ester using response surface methodology. *Bioresour Technol.* 2009;100:25-30.
32. López Granados M, Zafra Poves MD, Martín Alonso D, Mariscal R, Cabello Galisteo F, Moreno-Tost R, et al. Biodiesel from sunflower oil by using activated calcium oxide. *Appl Catal B*; 2007;73:317-26.
33. AOCS. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, AOCS Press, Washington, DC; 1993.
34. Gryglewicz S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Bioresour. Technol.* 1999;70:249-253.
35. Cheng J, Li Y, He S, Shen W, Liu Y, Song Y. Reaction kinetics of transesterification between vegetable oil and methanol under supercritical conditions. *Energy Sourc. Part A*, 2008;30:681-688.

36. Alamu OJ, Waheed MA, Jekayinfa SO. Alkali catalysed laboratory production and testing of biodiesel from Nigerian palm kernel oil. *Agric. Eng. Int: CIGR EJournal Manuscript Number EE07009*, 2007;IX:1–10.
37. Leung DY, Guo Y. Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process. Technol.* 2006;87:883–890.
38. Charoenchaitrakool M, Thienmethangkoon J. Statistical optimization of biodiesel production from waste frying oil through two-step catalyzed process. *Fuel Process. Technol.* 2011;92:112-118.
39. Wang ZM, Lee JS, Park JY, Wu CZ, Yuan ZH. Optimization of biodiesel production from trap grease via acid catalysis, *Korean J. Chem. Eng.* 2008;25:670–674.
40. Encinar JM, Gonzalez JF, Rodriguez-Reinares A. Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel, *Ind. Eng. Chem. Res.* 2005;44:5491–5499.

© 2013 Aworanti et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sciencedomain.org/review-history.php?iid=183&id=11&aid=933>